Synthesis and Characterisation of some Electroactive Polymers

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This thesis is dedicated to my parents.

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Declaration

This thesis has not been submitted as an exercise for a degree at this or any other University. Except as otherwise indicated, this work has been carried out by the author alone.

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Abstract

In order to synthesise suitable starting materials for the synthesis of electroactive monomers, the mono-methylation of some primary amines was firstly investigated. This methylation reaction involved a Mannich reaction of primary amine with succinimide and formaldehyde followed by the reduction using sodium borohydride in DMSO. This reaction was applied to p-dimethylaminoaniline, p-diaminobenzene, o-diaminobenzene and 1-aminoanthraquinone.

Three electroactive monomers, 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate, 2-(p-dimethylamino-N-methylanilino)ethyl acrylate, and 4-(p-dimethylamino-N-methylanilino)butyl acrylate were synthesised through the tosylation of certain hydroxy alkyl acrylates followed by nucleophilic substitution with p-dimethylamino-N-methylaniline.

Homopolymers of the three electroactive monomers and copolymers of the electroactive monomers with methyl acrylate and styrene, with different compositions, were synthesised through free radical polymerizations. The characterization of these polymers by NMR gave interesting stereochemical informations of the polymer chain.

The electrochemical properties of these electroactive polymers were investigated both in solution and in solid state (as modified electrodes) using cyclic voltammetric experiments. According to the electrochemical behaviour of these polymers in different conditions, some good electrolyte systems (TEAP or Lithium perchlorate in propylene carbonate) and potential range (-0.3 to 0.5V vs. SCE) were suggested for the applications of these polymers.

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Chapter I

General Introduction

1.1 Background

There has been tremendous amount of interest in electroactive organic materials in the last two decades. Many kinds have been developed and they can be generally classified into three groups:

(a) conducting polymers: conjugated along the polymer backbone, and highly conductive when doped;[1, 2]

(b) donor-acceptor complexes: with electrical conductivity ranging from insulating to superconducting;[3,4, 5]

(c) redox polymers: redox active centres are contained in the polymer and they can be oxidized and reduced electrochemically.[5, 6 , 7, 8]

The relationship between the three categories is close. Sometimes their properties and applications are so similar to each other that it is hard to separate one from the other. For example, once the conducting polymer polyacetylene is doped with a donor or an acceptor, its conductivity can increase by 5 orders of magnitude; the concentration of dopant in the polymer can be as high as 50%; some workers classify this doped polymer also as a donor-acceptor complex.[9] Polyaniline and polypyrrole are classified as conducting polymers in this thesis, though they have been classified as redox polymers by some other authors.[10]

This introductory chapter provides an overall view of electroactive materials in general. Section 1.2 reviews the conducting polymers' synthesis and applications, in section 1.3 the development of donor-acceptor complexes is reviewed, and in section 1.4 the synthesis and applications of some redox polymers[11] are discussed. Section 1.5 introduces the reasons for choosing redox polymers for study.

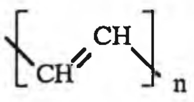
1.2 Electrically conductive polymers

1.2.1 Development of electrically conductive polymers

Polymers with conjugated π-electron backbones display unusual electronic properties such as low energy optical transitions, low ionization potentials, and high electron affinities. The result is a class of polymers which can be oxidized or reduced more easily and more reversibly than conventional polymers. Charge-transfer agents (dopants) effect this oxidation or reduction and in doing so convert an insulating polymer into a conducting polymer with near metallic conductivity in many cases. Conducting polymers represent an important research area with diverse scientific problems of fundamental significance and the potential for commercial applications.

The two key developments in the early stages of conducting polymer research were the discovery of a synthetic route to freestanding high quality films of polyacetylene (1) (PA)[9] and the discovery that these films could be doped by electron donors or acceptors to conductivity levels (1000S/cm) approaching those of some metals.[12] The conductivity of doped polyacetylene is comparable to the highest values achieved in any organic system, ie, those highly ordered organic charge transfer crystals. This comparison is significant since it demonstrates that the high degree of disorder that is clearly present in polyacetylene and most other polymers does not necessarily preclude high conductivity. It is the ultimate goal of this research to combine the processibility and other attractive properties of polymers with the electronic properties of metals or semiconductors.

A significant breakthrough occurred in 1979 with the discovery that poly(p-phenylene) (2) could also be doped to high conductivity.[13] It demonstrated that polyacetylene is not unique and led to a number of new polyaromatic-based conducting systems, including poly(p-phenylene sulfide) (3),[14] polypyrrole (4),[15] polythiophene (5),[16] and polyaniline (6).[17]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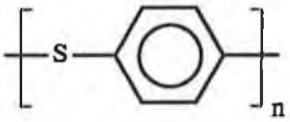
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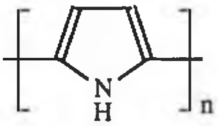
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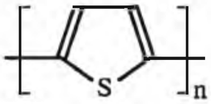
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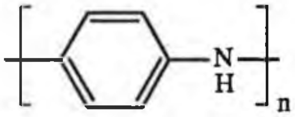
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Another important development was the discovery of conducting polymer solutions. The first system was poly(p-phenylene sulfide) doped with AsF_5 (a strong oxidizing agent) and dissolved in AsF_3 solvent. Films with high conductivity and mechanical integrity can be cast from these solutions. Though this particular solvent system is exotic and perhaps too delicate for commercial applications, this work represents the first demonstration of the feasibility of solution processing to form conducting polymer films.[18] Composites and blends are also being investigated as a means for processing and shaping conducting polymers for further application.[19]

1.2.2 Synthesis and properties of polyacetylene

In designing polymer syntheses, the incorporation of extended π-electron conjugation is of foremost importance. The monomeric starting materials are therefore typically of an aromatic or multiple carbon-carbon bond constitution that must be preserved in the final polymer backbone. Alternatively, conjugation can be achieved in a subsequent step that transforms the initial polymeric product into a conjugated polymer.

Polymerisation of acetylene yields a product of conjugated ethylene units (polyacetylene) (1). Although polyacetylene was first produced from acetylene by Ziegler-Natta catalysis, it generated little interest, because it was in a powder form.[20] It was important for the study of conductive organic polymers to find a synthetic method to produce coherent polyacetylene films which provide experimentalists with the physical form necessary to optimize detection of electronic and optical behaviour resembling that of metals.

In 1974, a method for the catalytic polymerisation of acetylene to yield free-standing films of polyacetylene of high mechanical strength became available.[9] The films were afforded by exposure of acetylene gas to smooth surfaces wetted with a solution of the Ziegler-Natta polymerisation catalyst at -78°C. After a period a coating with a metallic sheen appeared on the wetted surface It was easily removed to provide a good quality polyacetylene film (Shirakawa PA). It was subsequently reported[12] in 1977 that doping of these films by electron donors or acceptors yielded room temperature conductivities of the order of 1000S/cm.

polymerisation of acetylene at -78°C yields cis-PA, whereas polymerisation at higher temperature yields the more stable trans-PA (fig. 1.1). Alternatively cis-PA can be isomerised to trans-PA by heating at 150-200°C, or by chemical or electrochemical doping at room temperature.[9, 21]

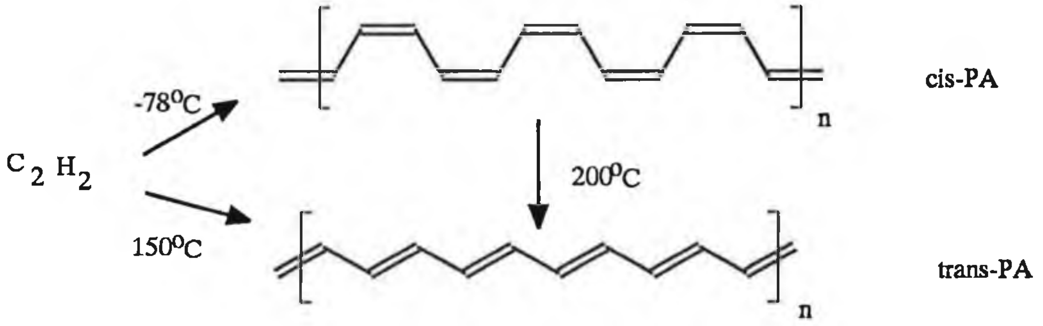


Figure 1.1 Cis- and trans-polyacetylene

Because of its extensive conjugation, PA is readily oxidised or reduced and consequently chemical doping can be achieved in either of two ways (fig. 1.2 and fig. 1.3).

Treatment with an electron-accepting species (an oxidant such as AsF_5 or I_2) yields p-doped PA (fig 1.2), in which monovalent anions and a polycarbocation are formed.

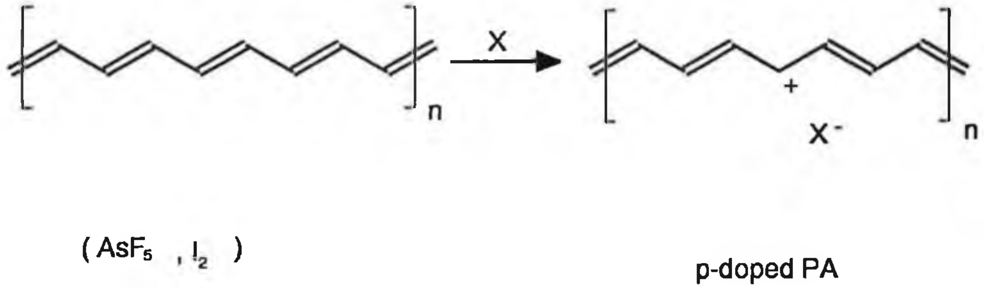


Figure 1.2 p-Doped polyacetylene

Conduction in the p-doped polymer involves positive charge carriers, with cationic centres migrating along the polymer chain. Alternatively, treatment with an electron-donating species (a reductant such as sodium naphthalide or lithium) yields n-doped PA (fig. 1.3), in which monovalent cations and a resonance-stabilised polycarbanion are formed. Conduction in the n-doped PA involves negative charge carriers, with anionic centres migrating along the polymer chain.

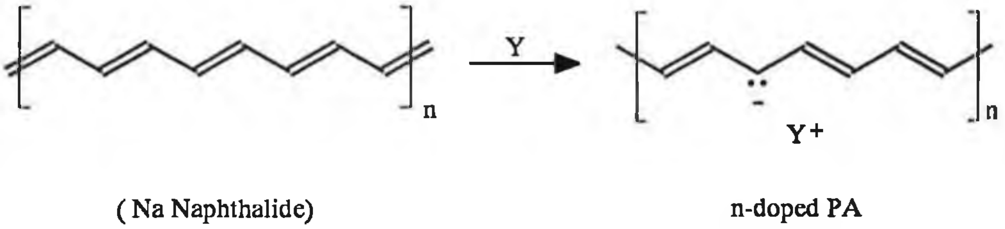


Figure 1.3 n-Doped polyacetylene

The role of doping in such systems is perhaps best understood as involving a charge-transfer interaction between PA and the dopant, the actual degree of charge-transfer (determined both by the nature of the dopant and its concentration) being important in determining the conductivity of the doped polymer. Doped polymers such as PA, in which the concentration of dopant can be quite high (50% by weight is not uncommon), are in reality conducting polymeric charge transfer complexes.

Electrochemical doping of PA was demonstrated in 1979, this work has since been expanded due to considerable commercial interest in the application of conducting polymers as electrodes in rechargeable batteries.[22]

There are a number of pathways which contribute to the transport of charge through PA, and related conducting polymers. Whilst transport along the polymer chain is efficient, the PA chains are interrupted by defects at intervals. This necessitates "hopping" of the charge from chain to chain. In addition PA films are composed of bundles of fibres with significant void volume, requiring transport of charge between bundles.

If better orientation of the polymer chains could be achieved, improvement in conductive performance might be anticipated, in addition to the realisation of the intrinsic anisotropy which should result from the extended π-system on parallel chains and the weak interactions between adjacent chains. Successes in this direction have been achieved, with methods having been developed for drawing of the PA films during the polymerisation process using modified catalysts. However processability of PA produced by Ziegler-Natta catalysis is difficult and has been a major factor in limiting its development. In addition, doped PA tends to be unstable in air, possibly due to reaction with water and oxygen, and this tends to limit its potential applications.[2]

The electroactive nature of PA was first demonstrated with thin films cast on a platinum surface.[23] The film can be switched between the neutral and the oxidised form at about 0.7V versus SCE in acetonitrile (eq. 1.1). The reaction is accompanied by a colour change from light yellow (neutral) to dark blue (oxidized) and a change in the electrical properties from insulating to conducting.

$$(CH)_m + A^- \rightleftharpoons (CH)_m^+ A^- + e^- \tag{1.1}$$

The electrochemical stoichiometry of the reaction is approximately 0.01 charges/repeating unit along the chain, and the reaction is accompanied by a large capacitative current. In the absence of air and moisture, the reaction is coulombically reversible and the material can be cycled repeatedly. The material is inherently sensitive to the atmosphere and any exposure immediately reduces the electroactivity and eventually destroys all the active properties of the polymer.[1]

Although the switching reaction is coulombically reversible, it is not simple. It is accompanied by structural reorganizations of the polymer and there are limitations to the diffusion of ions and electrolyte into the polymer strands. The peak height in the voltammogram scales linearly with sweep rate, but the peaks are not completely symmetrical and the positions of the oxidation and reduction peaks do not coincide. The current response for the first scan of a freshly prepared film is always larger than for the subsequent scans. Similar results are obtained with both the neutral cis and trans polymers.[23]

1.2.3 Synthesis and properties of polyaniline

In 1862, Lethely reported the formation of a dark green precipitate from the electrochemical oxidation of aniline in aqueous solution.[24] This material soon became known as "aniline black", and has been of intermittent interest to electrochemists. The interest has been both in the mechanic aspects of the reaction which produces "aniline black" as well as in the properties of the resulting material.[25]

Prior to 1980, the material at hand was primarily a powdery precipitate consisting of lower molecular weight oligomers including the octamer which could on occasion be solubilized. Studies were performed with the powdery deposit directly on the electrode or with pressed pellets. Polyaniline is electroactive, and switches in aqueous acid solutions in the potential range 0.1 to 0.8V anodic of the hydrogen electrode, producing broad oxidation/reduction waves in the voltammogram. The reaction is accompanied by a change in the conductivity of the material by a factor of 10^6. It was quickly recognized that this material could be useful in technological applications such as redox membranes with permselective properties and with sensitivity to pH, in charge storage and in electronic switches.

The redox reactions in neutral and acidic conditions[1] are shown in fig. 1.4.

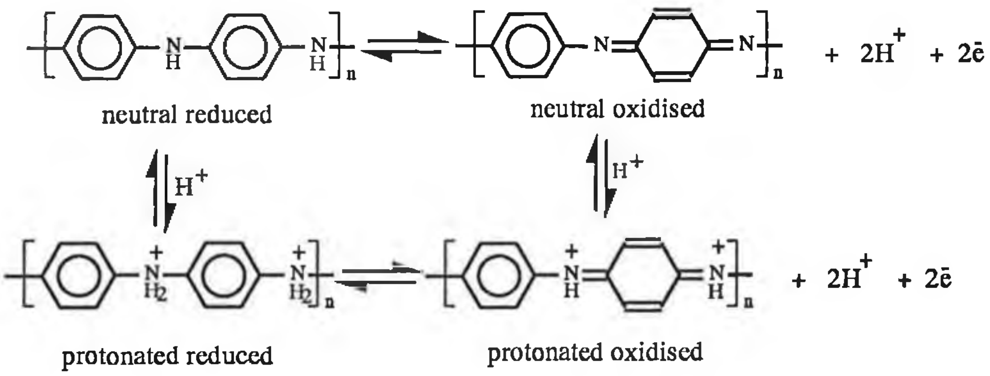


Figure 1.4

In 1980, a procedure was reported for the preparation of polyaniline as a thin and coherent film, by the electrooxidation of aniline in aqueous acid solution using a platinum electrode and with cycling of the voltage between -0.2 and +0.8V versus SCE. The general electroactive characteristic of the films are consistent with those of the powdery materials.[26]

The amount of faradaic charge involved in the oxidation reaction is 0.16 to 0.29 Faradays/repeating unit, and is often accompanied by a large capacitative current. This is a characteristic of all of the electropolymerized films which are electroactive and which switch from insulating to electrically conductive.

The fact that polyaniline is conveniently switched in aqueous acid solutions, and even in the presence of chloride and fluoride salts, is important to technological applications because it avoids the use of organic solvents.[27] The electroactivity of the film is not destroyed during storage in ambient conditions, in either the oxidized or neutral form. On the other hand, prolonged storage does make the material more resistant to oxidation and there is a ca. 100mV anodic shift in the switching potential.

In contrast to polyaniline, the other electroactive polymers in this class are not stable to moisture, air and halides such as chloride and fluoride.

1.2.4 Synthesis and properties of polypyrrole

Like "aniline black", "pyrrole black" has also been reported as a black intractable solid resulting from the oxidation of pyrrole, and much of the early work focussed on the chemical characterization and electrical properties of the material.[28] Unlike "aniline black", the early work did not include electrochemical studies and the switching properties of the material did not become known until recently[29]. Thus, there was little insight into the possible technological applications of this material. In 1980, the electrochemical generation of coherent films of polypyrrole on a platinum electrode was demonstrated. Pyrrole was polymerized electrochemically from its solution. Typically, application of a potential of 0.5V between two electrodes in an acetonitrile solution containing silver perchlorate electrolyte and pyrrole proceeds with the accumulation of an oxidized polypyrrole film on the anode. This film, as prepared, is conductive ("acceptor-doped"), since it incorporates inorganic counterions (in this example perchlorate anion) from the solution as it is oxidatively synthesized.[29]

Among other things, this permitted the investigation of the electrochemical characteristics of the film, and more generally, the study of conductivity of polymers in film form instead of pressed powder pellets. In contrast to the polymerized aniline films which are normally quite thin, relatively thick films of polypyrrole can be prepared by electropolymerisation. Furthermore, the properties of the film vary with the thickness, dividing the proposed applications into two categories, depending on whether the film employed is thin or thick. Thin films of polypyrrole are electroactive, thick films are mainly conductive and poorly electroactive.

Thin films of polypyrrole (less than 0.1 μm thick) are electroactive (fig. 1.5), and can be switched between the neutral and the oxidized state at about 0.1V versus SCE.

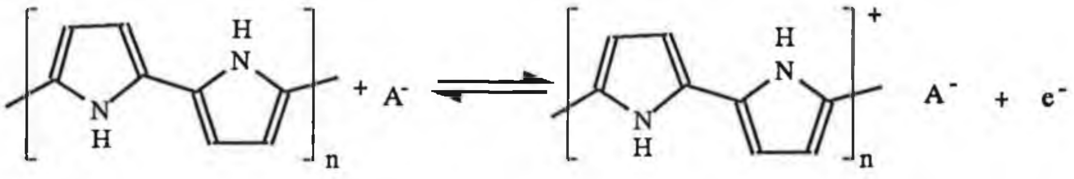


Figure 1.5

In aprotic solvents and in the absence of oxygen, the reaction is coulombically reversible and the film can be switched between the two oxidation states repeatedly without delay of the electroactivity. In the presence of oxygen, the electroactivity of the film decays slowly, and the film finally settles in a conducting form.[30]

For thicker films of polypyrrole, 0.2-2.0 μm thick, the switching characteristics are much less pronounced due to the slower migration of ions in and out of the film.[31]

Electrochemical polymerisation offers the advantages of homogeneous incorporation of dopant counterions into the polymer film as it is grown and of close control over the polymerisation parameters of current density and voltage. The method is limited, however, by the fact that the yield of polymer is restricted to the area of the working electrode in the electrochemical apparatus. For this reason, chemical syntheses are used when large quantities are required.[1]

1.2.5 Applications of conducting polymers

The projected commercial applications of conducting polymers are based on the promise of a novel combination of light weight, processibility, and electronic conductivity. Foremost among current commercialisation ventures is their application in rechargeable batteries.[2, 32, 33] Conducting polymers have also been proposed as promising new materials in circuitry elements.[33] An application with considerable commercial potential is electromagnetic shielding.[2, 35]

The advantages that a plastic conductor of electricity brings to these applications are numerous. For example, the facile processibility of polymers presents an improvement over traditional high temperature metallurgical processing. The light weight characteristic of plastics is expected to satisfy the low weight requirement of batteries for portable devices and vehicles. The main problems is the environmental stability. However, it is not a serious impediment to the development of commercial batteries employing conducting polymer electrodes since these are typically operated under sealed conditions.

Interest in the application of conducting polymers in rechargeable batteries began with the discovery of the electrochemical doping of polyacetylene. The electrochemical doping process constitutes the basic electrochemistry of the battery. The reversibility of electrochemical doping provides a rechargeable (or secondary) battery system. The "all plastic" or "double-polymer" battery has conducting polymers functioning as both cathode and anode. The redox reactions at the two electrodes are

$$\begin{array}{lllll} \text{Anode:} & P^{-}D^{+} & \underset{+\,e\text{-},\ \text{charge}}{\overset{-\,e\text{-},\ \text{discharge}}{\rightleftharpoons}} & P^{\circ} & + \quad D^{+}_{S} \\ \text{Cathode:} & P^{+}A^{-} & \underset{-\,e\text{-},\ \text{charge}}{\overset{+\,e\text{-},\ \text{discharge}}{\rightleftharpoons}} & P^{\circ} & + \quad A^{-}_{S} \end{array} \qquad (1.2)$$

where P^-, P^+ and P^0 represent the negatively charged, positively charged, and neutral polymer, respectively; A^- is the anionic dopant counterion, and A^-_S is its solvated counterpart in the electrolyte; D^+ is the cationic dopant counterion, and D^+_S is the solvated counterpart. Thus P^-D^+ corresponds to donor-doped polymer and P^+A^- to acceptor-doped polymer. Charging of the cell involves the electrochemical doping of the polymers; in the discharge process the doped polymers revert back to the neutral state. Note that the dopant counterions diffuse in and out of the polymer without change of oxidation state. This description of the basic electrochemistry of the battery has been confirmed by *in situ* spectroscopic studies.[36] The observed open-circuit voltages in a double-polymer configuration are 1.5 V for donor-doped polyacetylene versus acceptor-doped polyacetylene and 3.3 V for the analogous poly(p-phenylene) system.[37]

The double-polymer battery is not the only feasible configuration. In fact, battery cell configurations employing one conducting polymer electrode and one conventional battery electrode are most promising at this stage of development. For example, lithium metal can be used as the anode and a polymer electrode as the cathode.[38]

In a doped polymer-lithium cell, the redox reactions are

$$\text{Anode:}\qquad Li^{0} \underset{+\,e\text{-},\ \text{charge}}{\overset{-\,e\text{-},\ \text{discharge}}{\rightleftharpoons}} Li_{s}^{+}$$

$$\text{Cathode:}\qquad P^{+}A^{-} \underset{-\,e\text{-},\ \text{charge}}{\overset{+\,e\text{-},\ \text{discharge}}{\rightleftharpoons}} P^{\circ} + A_{S}^{-} \qquad (1.3)$$

At the anode lithium metal is oxidized to Li^+ during the discharge. The reverse process, reduction of Li^+ to Li^0, occurs on charging. The cathode reaction is the same as that in the double-polymer configuration: on charging the polymer is doped, on discharge the polymer returns to neutrality. The open-circuit voltages in this configuration are: 3.4V for lithium vs acceptor-doped polyacetylene and 4.2V for Li versus acceptor-doped poly(p-phenylene).[37]

In a cell employing lithium versus donor-doped polymer, electrochemical doping of the polymer occurs during the discharge cycle. The redox reactions for this configuration are

$$\text{Anode:}\qquad Li^{0} \underset{+\,e\text{-},\ \text{charge}}{\overset{-\,e\text{-},\ \text{discharge}}{\rightleftharpoons}} Li_{s}^{+}$$

$$\text{Cathode:}\qquad P^{\circ} + Li_{s}^{+} \underset{-\,e\text{-},\ \text{charge}}{\overset{+\,e\text{-},\ \text{discharge}}{\rightleftharpoons}} P^{-}\,Li^{+} \qquad (1.4)$$

The anode reaction is the same as described above. Open-circuit voltages in this configuration are generally lower: 1.0V for Li versus Li-doped polyacetylene and 0.4V for Li versus Li-doped poly(p-phenylene). All three battery configurations have been investigated for polyacetylene and poly(p-phenylene).[37] Polymers not amenable to donor doping, such as polypyrrole, can function only as cathode materials with, for example, lithium metal as the anode.

The potential advantages that conducting polymers offer over conventional materials as rechargeable battery electrodes are high gravimetric energy densities for maximum energy storage, high gravimetric power densities for rapid access to the stored energy, high conductivities for efficient current collection, large surface area for efficient materials utilization and high reaction rates, novel cell geometries, and low cost. A potential problem for conducting polymer batteries is the relatively low volumetric energy and power densities which can be attributed to the low densities of the polymers compare to conventional battery materials (for example, lead).[1, 2]

For successful application of conducting polymers in batteries, cycle life and shelf life must be improved. The former refers to the number of cycles the battery can undergo at a specified depth of discharge without significant deterioration in performance. Though commercial requirements for cycle life vary with application, 500 cycles is a reasonable target. The cycle life achieved thus far for acceptor-doped polymer electrodes is typically 50 cycles before failure or significant loss of capacity. The principle has been demonstrated that electroactive plastics can function effectively as battery electrodes. Work continues in the development of the prototype plastic battery from laboratory to marketplace.[1, 2]

A ramification of the electronic conductivity of these materials is their ability to absorb energy at low frequencies. This absorption of low-frequency electromagnetic radiation constitutes the basis for the use of conducting polymers as shielding barriers against electromagnetic interference. The homogeneous conductivity of conducting polymers would give better shielding than particulate conductivity where gaps may occur. Thus, the requirement that the barrier be both easily fabricable and responsive to electromagnetic radiation can be fulfilled by conducting polymers.[35]

Electronic circuitry is an obvious area for the exploitation of the electronic properties of conducting polymers. These plastics could be incorporated into such components as resistors, capacitors, and diodes.[34]

1.3 Donor-acceptor complexes

1.3.1 Introduction

In 1954, Japanese workers reported that an unstable perylene-bromine salt was conducting,[36] and during the 1960s many salts of tetracyano-p-quinodimethane (TCNQ) were found to be organic semiconductors.[39] Thus the foundations were laid for the discovery, in 1973, that the crystalline 1:1 charge transfer (CT) complex formed by the donor tetrathiafulvalene (TTF) and the acceptor TCNQ exhibited metallic behaviour.[40] This was a fulfilment of the prediction made in 1911 that organic solids might exhibit electrical conductivity comparable with that of metals, and the science of organic conductors was now truly inaugurated.[41]

CT complexes were the first class of organic compounds to display high electronic conductivity.[3] They are typically highly crystalline solids and are formed by the interaction of strong π-molecular electron donor and electron acceptor molecules. Beside electronic conductivity, these materials can exhibit photoconductive behaviour, light-initiated electron transfer from donor to acceptor leading to enhanced conductivity.[42]

1.3.2 Structure considerations

In donor-acceptor complexes exhibiting some degree of conductivity the involvement of molecular stacking in the crystal seems to be essential. Two types of stacking may occur (fig. 1.6).

DADADA	DADADA
ADADAD	DADADA
DADADA	DADADA
ADADAD	DADADA
Mixed stacks	Segregated stacks
Low conductivities	High conductivities

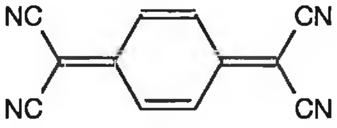
Figure 1.6 Mixed stacks and segregated stacks of donor-acceptor complexes

In mixed stacks electron localization on the acceptor leads to low conductivities. In segregated stacks, on the other hand, the donors and acceptors are sited to maximise π-overlap between adjacent molecules in the stacking direction, causing their unpaired electrons to be partially delocalised along these one-dimensional stacks. Thus an energy band is formed along the stacking axis, enabling them to conduct in this direction. The TCNQ-TTF molecular complex provides a classic example of a segregated stack.[43]

Donor-acceptor complex formation occurs by partial electron transfer from donor to acceptor, involving interaction between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor. The degree of charge transfer between donor and acceptor, determined by the ionisation potential of the donor and the electron affinity of the acceptor, determines the band filling in segregated stack complexes. If electron transfer is complete (resulting in a radical ion salt) the acceptor radical anion will then have one electron per molecule. Moving the electron along the chain (conduction) would then involve placing two electrons on the same molecule. Coulombic repulsion between the two negative charges would involve an increase in energy, so in practice a single electron remains associated with each molecule and the radical ion salt is a poor conductor. If, on the other hand, charge transfer is less than complete (in TCNQ-TTF it is approximately 60%) there will be some vacant sites to which electrons can move. Formation of a metallic band which is only partially occupied can then occur and the conduction process becomes much more energetically favourable.[3]

1.3.3 Synthesis of donors and acceptors

As a powerful π-molecular acceptor, TCNQ (7), has proved central to the development of conducting CT complexes and radical-ion salts. A great many complexes of TCNQ with various donors were found to be semiconductors.[39]



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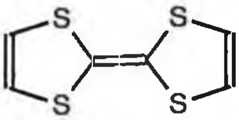
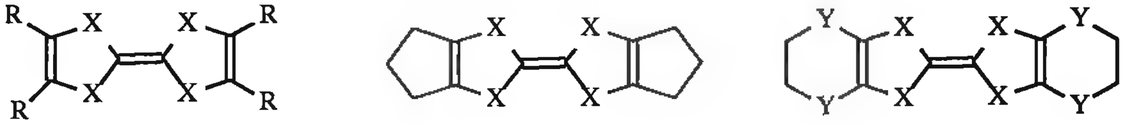


(8)

The preparation of a donor TTF (8) in 1970 led, two years later, to the discovery that the chloride salt of TTF had high electrical conductivity.[44] This in turn led in 1973 to the synthesis of the first truly "organic metal" when a complex of the donor TTF and acceptor TCNQ, in a 1:1 stoichiometry was found to be metallic at room temperature (σ_{rt} of 500Scm^{-1}) increasing to σ_{max} of approximately 10^{4}Scm^{-1} on cooling.[40] However the conductivity of the complex rapidly decreased on cooling below 59K where it became semiconducting, undergoing a metal-insulator or Peierls Transition. In the simplest term, a Peierls Transition occurs where the conducting chain is stretched in one region and contracted in another, so that the conducting electrons become localised, with a filled electron band at a lower energy and an empty band at a higher energy, i.e. the distortion leads to a band gap which results in an insulating or, at best, a semiconducting material at low temperature.[3]

Since the discovery of high electrical conductivity in the TTF-TCNQ complexes there has been unabated interest in the creation of new donors. Much of the work has centred on the addition of substituents onto the TTF skeleton either in place of its hydrogen atoms or by substitution of other hetero-atoms such as selenium and more recently, tellurium in place of its sulphur atoms (fig. 1.7). The greater spatial extent of the p- and d- selenium (and tellurium) based orbitals leads to larger intrachain bandwidths and hence increased metallic conductivity in addition to favouring increased interchain interactions, thereby supressing any Peierls distortions.[3, 42]



X	R	
S	H	TTF
Se	H	TSF
S	Me	TMTTF
Se	Me	TMTSF
Te	H	TTeF

X = S	HMTTF
X = Se	HMTSF

X	Y	
S	S	BEDT-TTF
S	O	BEDO-TTF
Se	Se	BEDS-TSF
S	Se	BEDS-TTF

Figure 1.7 Some donors

The first of these "organic metals" not to undergo a Peierls transition was HMTSF-TCNQ which has a conductivity in excess of $10^3 Scm^{-1}$ down to the lowest temperatures.[45] This was followed by the observation of superconductivity under pressure in the tetramethyltetraselenafulvalene-phosphorous hexafluoride salt, $(TMTSF)_2PF_6$, in 1980 at T_c =1K under

1.2Kbar pressure.[46] Superconductivity has since been discovered in many TMTSF salts. The highest temperature for the onset of superconductivity in an organic material is 12.5K reported for $(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$ salt.[47]

In comparison to new donors there have been very few new acceptors developed over the last decade. This is partly because the synthesis of many TCNQ derivatives is not easy to accomplish, unlike their TTF analogues. In general, substitution on the basic TCNQ skeleton results in complexes that are less conducting than those of TCNQ itself.

1.3.4 Polymeric CT complexes

Much interest has been generated in macromolecular CT complexes since the discovery of high electronic conduction in their low molecular weight analogues. The goal was to develop polymeric materials which might be anticipated to incorporate the desirable conductive characteristics of their low molecular weight analogues without the brittleness and lack of strength which characterises the crystalline materials.[4]

Most polymeric complex systems rely on the incorporation of pendant donor and acceptor groups along the polymer backbone. A number of possible arrangements arise, each relying on the development of charge transfer between the donor and acceptor groups within the polymer and hence endow it with the conductivity and photoelectric characteristics of simple CT complexes (fig. 1.8). Alternatively donor and acceptor groups can be built into the polymer structure, i.e. as in-chain groups such as in condensation polymers.

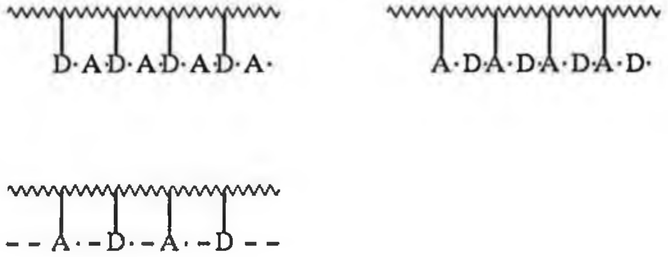
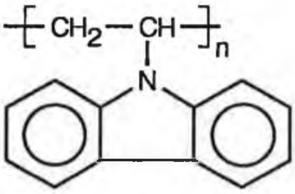


Figure 1.8 Some combinations of polymer donor-acceptor complexes

The most widely studied combination is that involving a polymeric donor and a low molecular weight acceptor. The situation pertaining in such polymers is much more complex than for their low molecular weight crystalline models. The interactions between donor and acceptor components are strongly influenced by the conformational freedom within a given polymer backbone as well as the precise configurations of the pendant interacting groups. The overall result is that the extended stacking microstructure, which is so characteristic of low molecular weight crystalline donor-acceptor complexes and critical for electrical conductivity, cannot normally evolve. Consequently, while these polymer donor-acceptor systems do exhibit enhanced conductivities over and above those shown by the polymer alone, their conductivities are generally much lower than those of the corresponding monomeric complex.

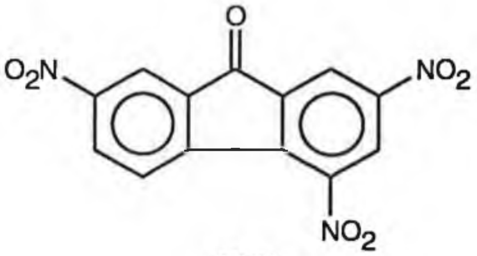
1.3.5 Applications of donor-acceptor complexes

In view of their successful commercial exploitation it is not surprising that polymers incorporating the electron-donating carbazole moiety have been most extensively studied, particularly poly(N-vinylcarbazole) (PVK) (9). The complexes formed by incorporation of trinitrofluorenone (TNF) (10) into PVK are photoconductive and this combination provided the first commercial organic photoconductors, widely used in early photocopying processes.



PVK

(9)



TNF

(10)

The surface of a drum, coated with the photoconductive material, is charged by a corona electrical discharge in the dark. It is then exposed to a bright image reflected from the original. Where the light falls, the material become conductive and the charge leaks away to the underlying earthed drum. The dark areas retain their charge, and the image is developed by the attraction of toner (dry ink) to the charged areas, followed by its transfer to a sheet of paper. The photoconductor is then cleaned of toner, any remaining charge is removed by exposure to an erase lamp and the photoconductor is again ready for recharge.[48]

Charge transport mobilities in the PVK/TNF system are no longer sufficient to satisfy the requirements of modern high speed copiers and laser printers and it has been replaced by superior, but closely-related, acceptor-doped donor polymers.[4]

Another important example, from a technology applications stand point, is the perylene-iodine complexes which have been developed successfully and are currently used in long-life pacemakers. This material is used as a cathode in a cell containing lithium iodide solid electrolyte and a metallic lithium anode. The cell has an open circuit potential of 2.81V and a projected decay of 2V after 12 years. This type of cell which does not liberate gases, offers the advantage that leaks and separator failures are minimized.[49]

Electrode applications have also been considered for some other donor-acceptor complexes. TCNQ-TTF complex was used as pressed pellet electrodes in aqueous solutions, and in acetonitrile. In both solvents, the working range is restricted by the redox chemistry of the TTF-TCNQ salt. The compex is stable in water for periods of several weeks, and in electrolytic solutions with most electrolytes except chlorides and bromides. The cyclic voltammograms for the $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ and Cu(II)/Cu(I) reactions measured with these electrodes are similar to those measured with a platinum electrode. TCNQ complexes with other donors were also probed for electrode applications.[50]

1.4 Redox polymers

1.4.1 Introduction

Redox polymers are high molecular weight substances that can transfer or accept electrons from their surroundings.[51] The idea to produce and use synthetic polymers with such properties was first realized during 1943-1944.[52] Redox polymers are essential elements of every kind of biological material because of their connection to the fundamental processes of life, i.e. energy conversion, transport, and storage. In biological systems, different redox polymers are often combined into complex organized assemblies. As in biochemical research, it is the aim of redox polymer research to construct suitable and simple systems capable of performing the above mentioned processes.

The redox function is usually organic (eg, hydroquinone/quinone system), but inoganic systems are also used, (eg, ferrocene, $Ru(bipy)_3^{3+}$). The redox function is bound to the polymer matrix by means of covalent, ionic, or adsorptive bonds. In the case of ionic bonds, the term redox ion exchanger is commonly used. However, most redox polymers contain covalently bound redox groups. Formerly, the polymers had different names: electron exchanger, redox exchanger, electron exchange polymer, oxidation-reduction polymers and redoxite.[6]

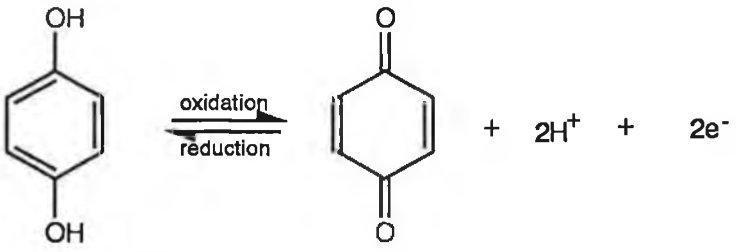
A variety of synthetic methods exists for the preparation of redox polymers. These may be divided into two classes: methods for preparing the desired polymers by polymerisation of the appropriate monomers, and methods whereby preformed polymers are chemically modified. Both methods permit the synthesis of polymeric structures with many sites capable of accepting or donating electrons. The redox group may form part of the polymer backbone, or may be attached as substituents on the backbone of the polymer. Redox polymers of the first type exhibit effects due to the constraints of being part of the backbone as compared to the latter type where the redox group is a substituent on the backbone. In addition, differences in chemical and physical properties may be expected between linear polymers, which may be put in to solution, and crosslinked polymers which are insoluble, but which may become solvated and accessible to reaction. Also, crosslinked polymers have a number of physical properties that influence their redox behavior.

Certain fundamental considerations affect the choice of the overall synthetic route to a redox polymer. Initially, investigators picked the route starting with monomer despite the difficulties in synthesis and the overall low yields. Monomer synthesis, followed by polymerisation, has the advantage that the composition of the product is known with increased certainty, and that the product is readily characterized. At the same time, the advantages of starting with preformed polymer and attaching redox groups to it have been apparent, especially when considerations of yield, total capacity, and cost were uppermost. It has been reported that limited solubility, side reactions, and crosslinking may cause some difficulties in the chemical modification of high polymers.[7, 53, 54]

1.4.2 Addition polymerisation

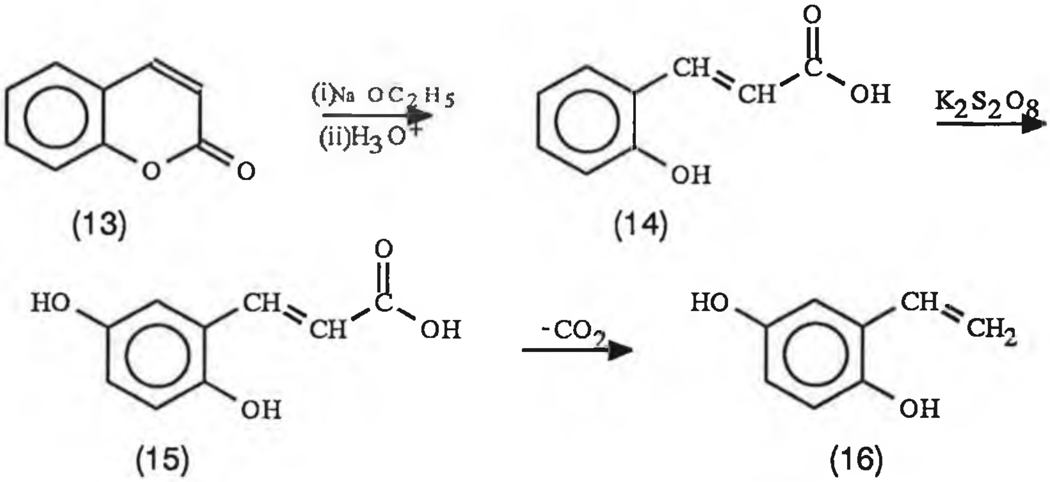
1.4.2.1 Vinylhydroquinone and derivatives and their polymers.

The redox active group in this kind of polymers is the hydroquinone/quinone system, (eq. 1.5), it is known to be rapidly reversible, and a great deal of fundamental work has been done with this system.[55]



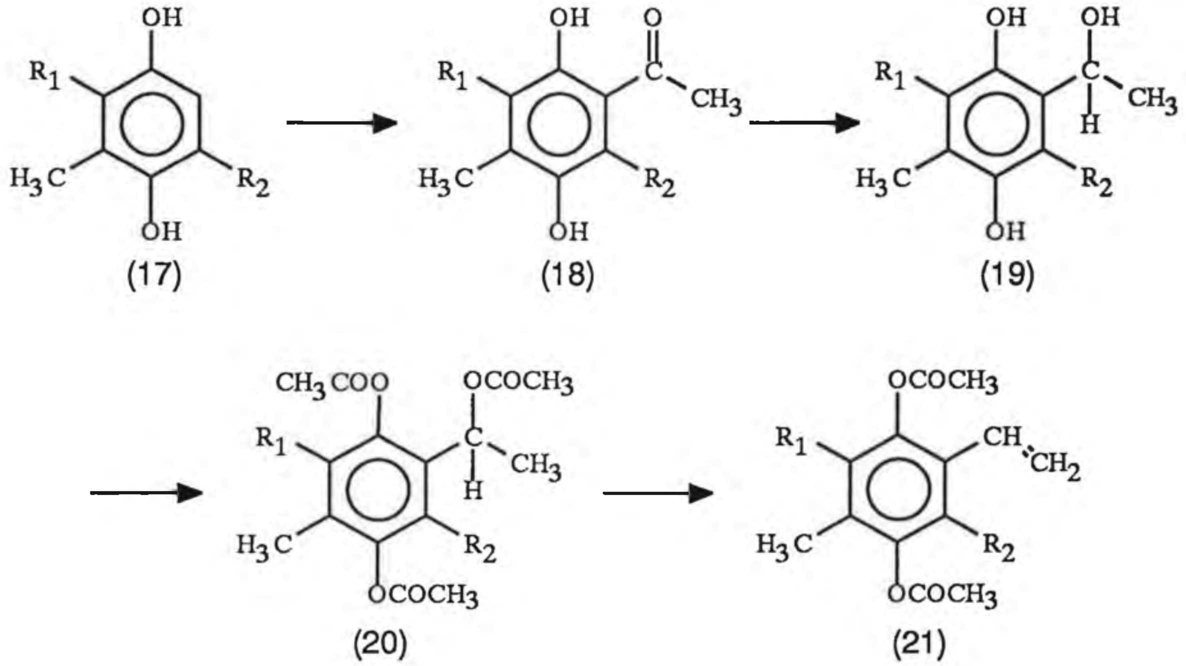
(11) (12) (1.5)

Vinylhydroquinone was first prepared by Updegraff and Cassidy by the hydrolysis of coumarin (13) to o-coumaric acid (14), according to the procedure of Ebert. Treatment of the acid (14) with potassium persulphate gave 2,5,-dihydroxycinnamic acid (15) which, upon decarboxylation by heating at reduced pressure, yielded 2-vinyl-1,4-hydroquinone (16).[56]



Although in the absence of oxidants the polymerisation of styrene is not affected by hydroquinone, the polymerisation of the monomer above with radical or ionic initiators led only to oligomers.[57] On the other hand, quinones with a redox potential of $E_0 = 600 \pm 300$ mV, e.g. p-benzoquinone, are effective polymerisation inhibitors. The protection of the OH-function in hydroquinones, for instance by esterification (acetates, benzoates), yields compounds that can be polymerized without difficulty; protecting groups are removed hydrolytically.[56]

All isomeric methyl-substituted vinylhydroquinones (protected as acetates) (21) have been synthesized via pyrolysis of intermediates containing the 1-acetoxyethyl group (20).[58]

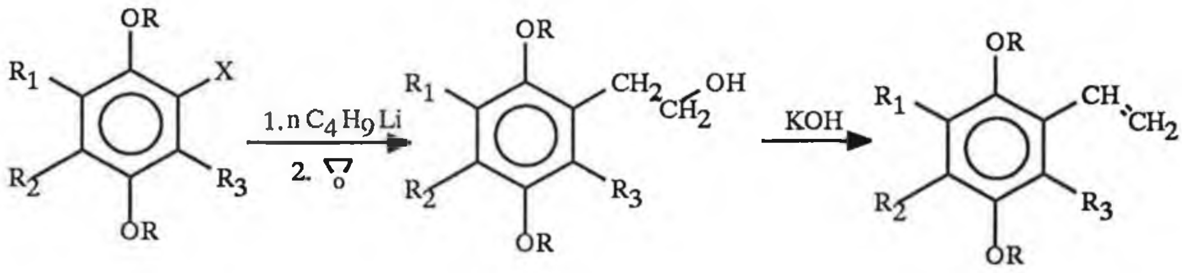

(17) (18) (19) (20) (21)

R_1 = H, CH_3

R_2 = H, CH_3

The monomers with a free meta position with respect to the vinyl group polymerize easily.

In another method, the hydroquinone, protected as a bisacetal (22), is metalated by n-butyllithium and the product reacts with oxirane or acetaldehyde. The primary or secondary alcoholic function is dehydrated; monomers (24) are polymerized by a free-radical mechanism. The protective group is removed quantitatively by acid under mild conditions. When there is a CH_3O- linkage in the acetal, formaldehyde is obtained; it may react with the hydroquinone units of the polymer producing cross-links.



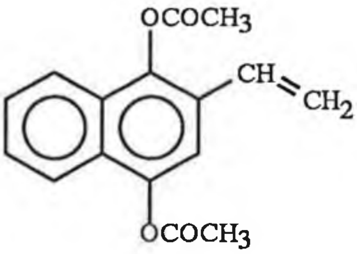
(22) (23) (24)

R_1 , R_2 , R_3 , = H , CH_3 R = CH_2OCH_3 or $CH(CH_3)OC_2H_5$

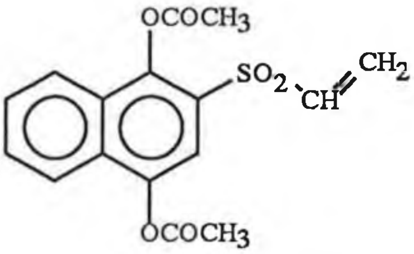
X = H , CH_3

Therefore, the ethyl acetal linkage is the preferred protective group because it hydrolyzes to the less reactive acetaldehyde. Complicating side reactions are caused by the introduction or removal of the following protective groups: acetate, benzoate, methyl ether, higher alkyls, and tetrahydropyranyl ether.[59]

Polymers with the naphthohydroquinone-naphthoquinone system have been synthesized via protected derivatives of naphthohydroquinone, e.g. two compounds (25) and (26)[60]

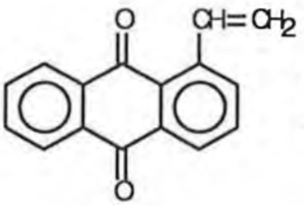


(25)

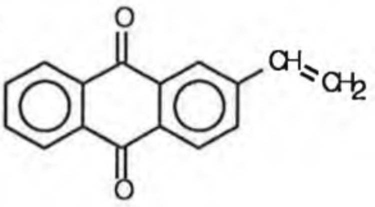


(26)

Protection is not necessary in the case of anthraquinone derivatives. Of the two isomers, 1-vinylanthraquinone (27) and 2-vinylanthraquinone (28), the latter copolymerized readily with styrene and divinylbenzene, like the more soluble 2-isopropenyl anthraquinone (29). The polymerisation of acrylic and methacrylic acid esters and amides of anthraquinone derivatives has also been described.[61]



(27)



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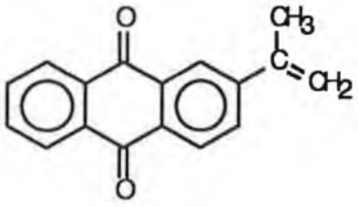
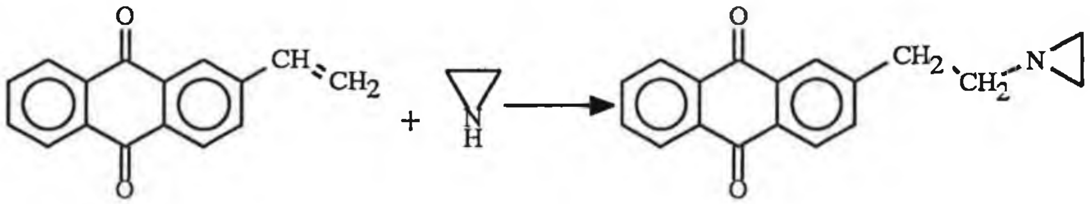


(29)

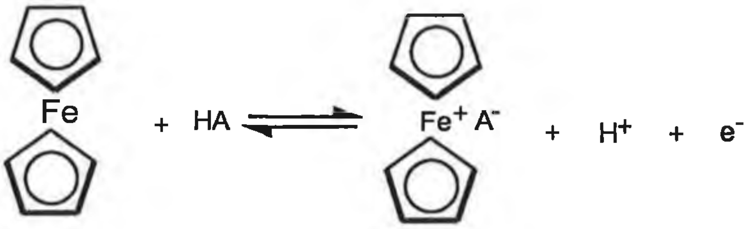
The addition of aziridine (31) to the double bond of anthraquinones (30) yields monomers (32) which homo- and co- polymerize cationically by ring opening.[62]



(30) (31) (32)

1.4.2.2 Vinylferrocene.

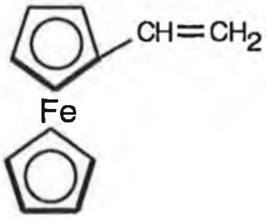
Dicyclopentadienyliron (ferrocene) (33) is a compound in which iron is linked covalently to two cyclopentadienyl groups in what has been called a "sandwich" structure. Among the metal chelates, ferrocene is one of the most characteristic representatives. This material is of interest because under suitable conditions, the iron can be reversibly oxidized to the trivalent form (34). Polymers containing ferrocene units, therefore, can be classified as redox polymers.



(1.6)

(33) (34)

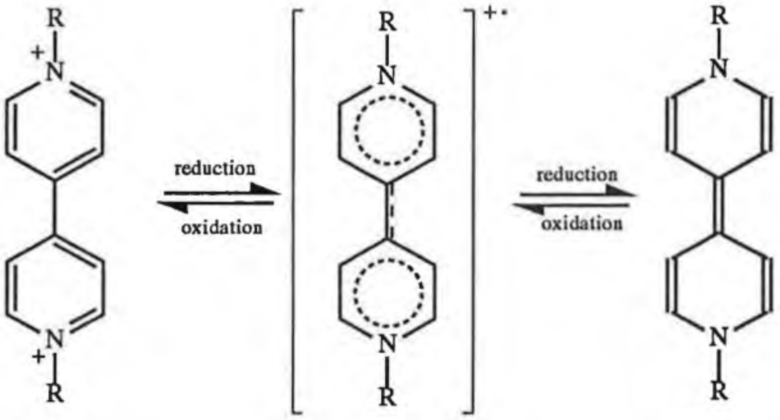
The polymerisation of 2-vinylferrocene (35), available commercially, has been described.[63] The properties of these redox polymers have been studied.[64]



(35)

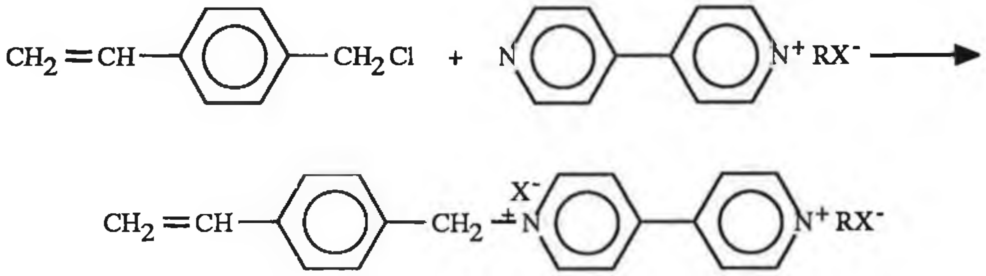
1.4.2.3 Viologen redox system

Viologens are colourless 4,4'-bipyridinium salts (36) which may be chemically or electrochemically reduced[65] through two separate reduction stages. The first reduction yields a deep violet radical cation (37) and the second forms a neutral red 1,1'-dialkyl-1,1'-dihydro-4,4'-bipyridyl (38).

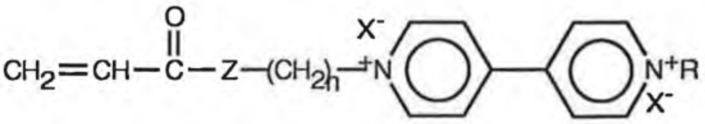


(36) (37) (38)

Some monomers containing viologen redox groups have been reported.[66] They can be styrene derivatives such as (39), the ester (40), and the amide (41). These compounds homo- and copolymerize by free radical initiation to yield high molecular weight product.[66]



(39)

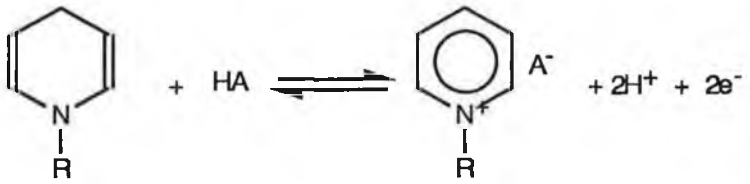


Z = O or NH

(40) (41)

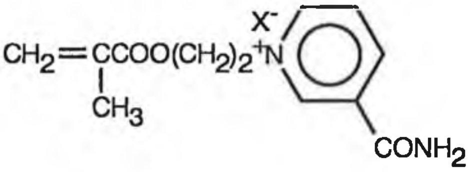
1.4.2.4 Dihydropyridine-pyridinium redox system

The dihydropyridine-pyridinium redox system is reversible.[10]



(42) (43) (1.7)

Most of the monomers containing this redox group were in the form of nicotinamide derivatives. For example the compound (44) can polymerize by free radical initiation. Polymerisation of some related systems in their reduced form yielded only oligomer.[66]

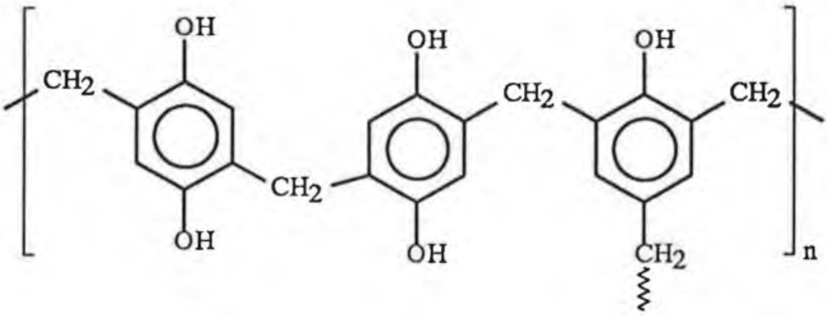


(44)

1.4.3 Step-growth polymerisation.

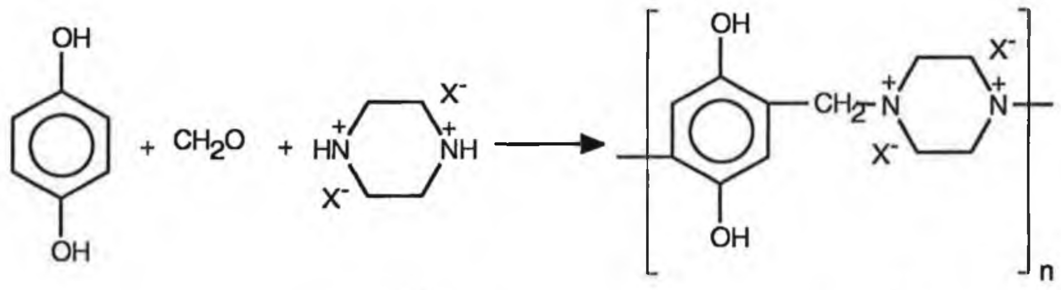
Polycondensation products are often prepared by simple methods starting with bi- or polyfunctional compounds; usually no protection of the redox system is needed. However, certain limitations in application of these redox polymers result from hydrolyzable functions in the backbone. Moreover, in most cases the redox system is part of the backbone, in contrast to addition polymers; in redox processes, the polymer structure is strongly affected.[10]

Most extensively studied are the hydroquinone or polyhydroxybenzene-formaldehyde condensates. In general, the condensation is catalysed by acid. In the first stage, bismethylol compounds are formed, in the second stage, linear polymers. Addition of phenol or cure at high temperatures results in cross-linking (45).[67]



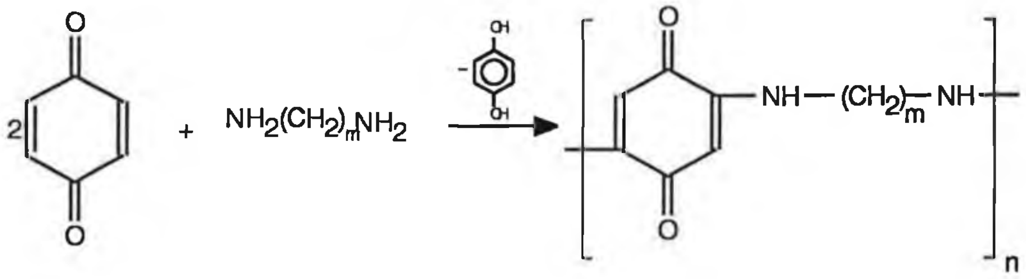
(45)

The Mannich condensation of piperazine (46) with formaldehyde and hydroquinone gives soluble linear polymers (47).[68]



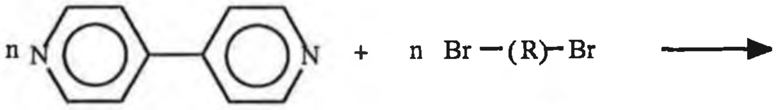
(46) (47)

Linear polyaminoquinones (49) are obtained from diamines (48) and benzoquinone.[69]

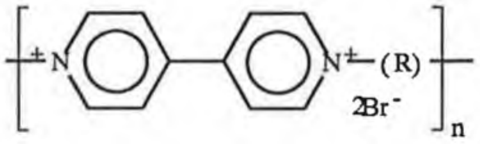


(48) (49)

Polyviologens (52) are prepared by polycondensation of 4,4'- bipyridine (50) with aliphatic dihalides (51). The water soluble linear polymers (52) showed polyelectrolyte properties; molecular weights up to 10^4 were obtained[65].



(50) (51)

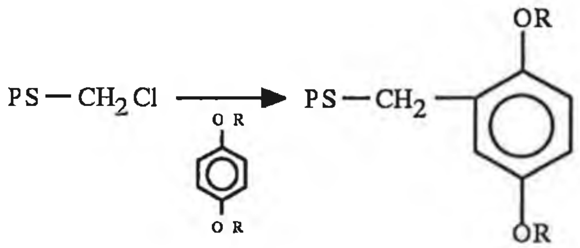


(52)

1.4.4 Polymer modification

The chemical modification of polymers is a well known technique. It offers the advantage of preserving many of the properties of the starting polymer. The functions introduced are pendant and are usually at positions accessible in subsequent reactions. On the other hand, these reactions seldom go to completion, and the products of side reactions usually remain.

The polymers of styrene, linear or cross-linked, are important starting materials. Introduction of the redox function onto the polymer may require several steps. Reactions of complete redox systems or their precursors with functionalised polymers are frequently successful, giving redox polymers. Poly(chloromethylstyrene) (53) reacts under Friedel-Crafts conditions with protected hydroquinone or free hydroquinone to give the appropriate redox polymers (54).[7]

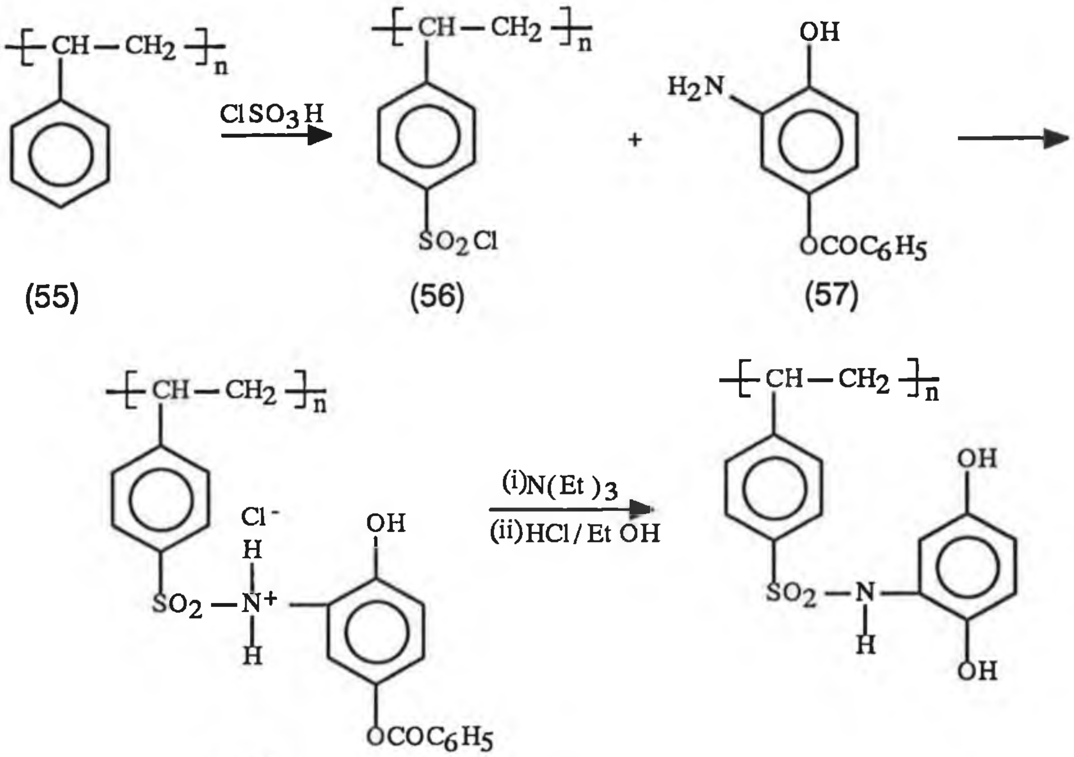


(53) (54)

PS = polystyrene

R = H, CH_3, $COCH_3$

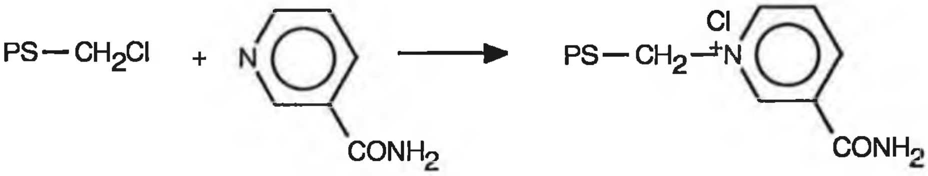
Redox polymers containing quinones bound by a sulfone bridge are prepared from poly(styrenesulfonic acid chloride) (56). Some hydroquinone sulfonamides (59) are synthesized by polymer-analogue reactions (see below).[7]



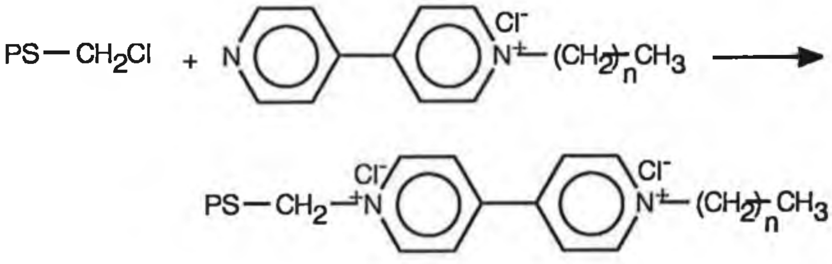
(55) (56) (57)

(58) (59)

The nicotinamide and viologen functions can also be introduced by reaction with a functionalised polymer to give for example, (60) and (61).[10]



(60)



(61)

1.4.5 Applications of redox polymers

The applications of redox polymers are naturally related to their chemical properties. The most important of these are : (a) acid-base, (b) redox, and (c) structure properties.

The acid-base properties have two aspects. Each redox functional group usually is, in one part of the redox cycle, a potential ion exchanger. Thus, polyvinylferrocene is not ionic, but when the iron is oxidized to the ferric form the redox polymer is a potential anion exchanger. In the hydroquinone form a hydroquinone-functionalised redox polymer is a potential cation exchanger. In the pyridinium form of a polyvinylpyridinium polymer, the polymer is a potential anion exchanger. This behaviour is important because such polymers, when their state of oxidation is changed, revert to non-ion exchangers. One has, therefore, a self-purging ion-exchanger system.[10]

But the acid-base property has another important aspect: through it the midpoint potential of the polymer may be influenced. Thus, an increase in pH decreases the potential of hydroquinoid systems while a decrease in pH raises the midpoint potential. Moreover, it follows that in a buffered system the potential can be held constant and, indeed, copolymers of vinylhydroquinone dibenzoate, vinylpyridine, and a vinyl ester have been prepared so as to yield self-buffering (weak-acid, weak-base) copolymers.[10]

Their specific redox properties are usually the chief reasons for applying these resins. There are available a wide range of midpoint potentials. Polymer potentials may range from the very low potentials exhibited by polymers such as polyvinylanthraquinone to the relatively high potential of poly(vinyl p,p'-dihydroxybiphenyl), and organic polymers of even higher potential may surely be made.[10]

Redox polymers can be prepared in many physical forms: soluble polymers, linear and crosslinked polymers as beads, dispersions, membranes, films, rods, and so on. The chemistry of the functional group is certainly altered to some extent by the fact that it is held localized on a polymer structure. The structure has other properties that make it important in various applications. For example, soluble polymers diffuse much less rapidly than monomer would under the same conditions, so that a polymeric colourformer or developer might help to maintain sharper edges to a photographic image, compared with a small-molecule colorformer or developer. Again crosslinked or insoluble redox polymers have the advantage that they could be used as reagents in a chemical reaction and then filtered off.[5, 7, 55]

As mentioned above, the behaviour and the application possibilities of redox polymer are determined by the redox potential of its redox systems and its inherently coupled acid-base properties; in addition, they are also strongly influenced by the morphology and the molecular structure of the redox polymer.

The stability of the redox functions and the polymer matrix are of particular importance. The acid-base properties of the redox functions are buffered by introducing suitable ionic groups into the matrix. By modifying the synthesis, solubility properties and morphology can be adjusted. For instance, in electrochemical applications, conductivity of the matrix and a high structure flexibility of the redox groups are required, permitting close contacts with each other. Therefore, for each application a tailor-made redox polymer is synthesized. In general, redox polymers are used as polymer reagents, but they have also been applied as electrochromic materials and redox catalysts and mediators.[5,10, 65]

1.4.5.1 Reagents

Redox polymer reagents offer the advantages of easy mechanical separation of regenerable reagents from products by filtration in batch techniques or flow in column techniques and the possibility of using excess reagent to shift the equilibrium toward the product.[53] These redox polymers are usually insoluble but swellable[54] they can be used both as reducing agent and oxidizing agent.

Redox polymers in the reduced form (hydroquinone form) have been used for the reduction of ions and for depositing metals. Using a poly(vinyl anthraquinone) polymer the following metals could be deposited by a batch process: silver from neutral silver nitrate solutions, copper from 2N sulphuric acid-Cu^{2+} solutions. The deposited metals could be dissolved without affecting the redox polymers.[7]

Many processes require water free of dissolved oxygen or other oxidizing species, e.g. chlorine. Redox polymers in the reduced form can remove oxygen from solution. Under laboratory conditions, such water can be prepared with redox polymers or redox ion exchangers by the column method. Leaking redox species are subsequently absorbed on a mixed-bed column.[7, 67]

The serious corrosion problems that may arise when water is heated in contact with iron or steel (as in commercial boilers) are thought to be related at least in part to the presence of dissolved oxygen in the water. The removal of this dissolved oxygen is considered desirable, particularly where high pressure is in use. Two general classes of processes are used to reduce the level of dissolved oxygen: mechanical deaeration and chemical reduction.

Mechanical deaeration is carried out by passing the water over heated surfaces. This may be done at atmospheric or reduced pressures. The deaerators remove oxygen down to about 1 ppm, which is still too high a concentration in today's high pressure boilers. By use of chemical additives, i.e., phosphites, sulfites, or hydrazine, the oxygen level is reduced even further;

however, residual salts or side products that increase the solid content or produce corrosive gaseous products may be formed. It was reported that by using redox resins obtained from the condensation polymerization of hydroquinone, formaldehyde, and phenol, a product was obtained that would remove oxygen from water without the addition of salts or other contaminants. The reduced form of the resin reacts with oxygen and is oxidized to quinone, while the resulting hydrogen peroxide would react with another hydroquinone unit to give quinone and water. This can be done using both fixed bed and batch techniques.[10, 70]

Redox polymers are also reactive in pure organic solvents. Applications for removing peroxides from ethers, protecting air-sensitive substances (polymer antioxidants), and stabilizing vinyl monomers and polymers have been described.[71] In preparative organic chemistry, redox polymers are employed as reducing or oxidizing agents. Anthraquinone-type redox polymers are used for the reduction of benzoquinone and the reductive cleavage of the 2-hydroxymethylanthraquinone ester group (carboxyl protection of peptides).[72]

1.4.5.2 application in digital display devices

The use of electrochromic materials is one of the methods by which display devices may be constructed. Redox polymers are presently finding applications in such devices. A colourless polymer may be reduced at electrode to yield a highly coloured derivative which can be "erased" upon electrochemical oxidation back to the colourless form.[65]

In this regard, colourless viologen dication (36) can be reduced to the deep violet radical cation (37) and the red neutral form (38). Both reduction states are rapidly reoxidized by molecular oxygen to the non-reduced dication species.[73] There have been several attemps to utilize viologens in electrochromic display devices.[74, 75]

Monomeric viologens, however, precipitate upon reduction to the radical cation species in electrolyte solutions. It is known that the cation radicals of viologens associate to form dimers, either monocation dimers or dication dimers.[76] Further, the second reduction step in monomeric viologens is often irreversible and results in poor display performance[77]. To overcome some of the problems inherent in systems using monomeric viologens, polymers based on viologens have been investigated. Spectroscopic analysis of polyviologens suggests that in the polymeric state there is still some intermolecular interaction between the radical cations of the reduced polymer. The stability of the polymeric viologens is however better than that of the monomeric species.[65]

Electrochromic polymers containing tetrathiafulvene and pyrazoline dyes were also attempted in electrooptic recording devices.[77] The colour change upon electroreduction is usually yellow to green; not as visually striking as the colour change apparent upon electroreduction of viologens.[78]

1.4.5.3 Photoredox processes in macromolecular assemblies

The photoredox behaviour of macromolecules, and ways in which polymers influence the photoconversion process in various light-driven redox systems, have been the subject of a number of investigations. Photoredox reactions of polymers have been studied as models of photosynthesis in plants, the aim being the utilization of solar energy for production of primary substances necessary for human survival. Foremost among the aims of the endeavours are the photoinduced splitting of water to hydrogen and oxygen.[65, 79, 80] Other efforts have centred on the construction of photovoltaic devices. In light-harvesting reactions involving polymeric assemblies, the polymer can assume either a primary or secondary role, that is, the polymer contains the chromophore or it participates in the light transduction process by means of a sensitizing agent.

The tris(2,2'-bipyridyl) ruthenium(II) complex is currently receiving a lot of attention as a photocatalyst for decomposing water by solar radiation.[81] Since water is transparent to visible light, hydrogen and oxygen evolution systems require some sensitization to visible output of the sun.

This sensitizer enjoys extensive popularity since the maximum absorption of the chelate is at 480 nm, which is the wavelength of maximum solar spectral intensity. The photochemistry and quenching of excited state of $Ru(II)(bipy)_3^{2+}$ complex has been examined.[82] The behaviour of $Ru(II)(bipy)_2^{2+}$ bound to poly(vinyl pyridine) (PVP) upon irradiation in methanol or aqueous acid solution is much like that of the unbound species. At ambient temperature the macromolecular sensitizers are observed to luminesce weakly in methanol and acid solutions, and much more intensely from frozen methanol solutions or from films of the polymer at room temperature. The polymeric complexes can be highly cross-linked and become insoluble in most solvents, but well suited for film casting.[83]

Polymeric viologens can function quite well as poly-acceptors in macromolecular electron relays in various light-driven water-splitting systems.[84] Progress has been made towards more efficient systems by preparing polymeric viologens which concentrate the photosensitiser and the multielectron redox catalyst in the domain of the electron mediator. One group of workers has shown that pendant viologens on a styrene-acrylamide copolymer are more effective as electron mediators during hydrogen production than their monomeric counterparts.[11, 84, 85]

1.4.5.4 Electrocatalysis

The ability of redox polymers to exchange electrons at electrodes allows various electrochemical applications. Electrocatalysis is in principle a very important electrochemical process of great industrial interest. With the help of electrode coatings containing active surface states, oxidation or reduction of substrates in solution can be carried out. The aim is to drive reactions selectively and/or efficiently at a modest potential. In comparision to electrodes of inorganic materials (metals or metal compounds), those of organic compounds are at present at a fundamental stage of research. Electrodes modified with organic materials may have the disadvantage of less stability, but they possess the advantage of a broad range of application due to great variation of the active species confined on the electrode. [6]

A very thin layer of electropolymerized viologen onto a gold minigrid is sufficient to impart electroactivity, e.g., in the reduction and oxidation of sperm whale myoglobin.[73] With the aid of an electrode modified with polyviologen, horse-heart ferricytochrome c was reduced,[86] and at a electrode covered with an redox polymer containing 1,4-benzoquinone groups, glucose oxidase and xanthine oxidase were oxidized.[6, 87]

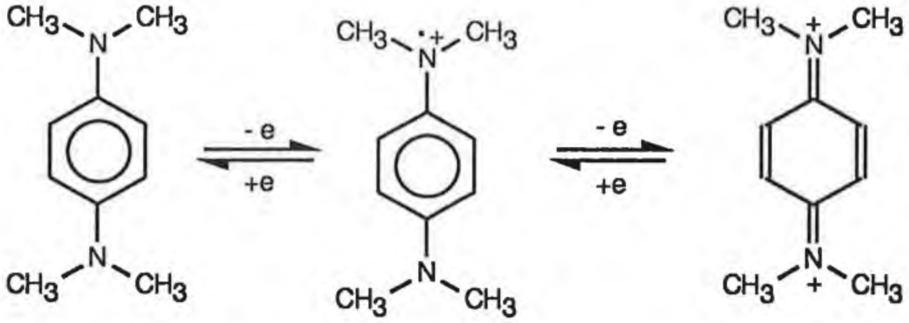
1.5 Background to the work described in this thesis

As can be seen from the earlier part of this chapter, polymers can be used as both electrode materials and as the electrolyte system (ion exchanging polymer). Scientists are working hard to achieve the "all plastic" or "solid state" battery. At this stage of development, the most promising configuration for a battery cell uses lithium metal as the negative electrode, and a polymeric material as positive electrode. Lithium metal is the lightest metal, and having the lowest electronegativity, it is ideal for the material of negative electrode. The normal potential of lithium to lithium cation is approximately -3 Volts[88], so it is in principle easy to get a high voltage rechargeable battery with lithium as the negative electrode.

Until a few years ago, all electrolyte systems were aqueous, and it was impossible to use lithium as a battery electrode material, because lithium reacts vigorously with water. The introduction of organic or water free electrolyte systems has made it possible to use lithium as the negative electrode and its use in conjunction with electroactive polymers as the positive electrode has been of much interest.

As part of a project funded under the EC BRITE programme, previous work in this department had been concerned with the design and investigation of redox-active.[89] VARTA Batterie (Germany), in conjuction with BASF, had been investigating the use of polyaniline. However there were problems inherent in the production of suitable material for battery purposes and alternative materials were sought.[89] Amongst those investigatigated at DCU was poly(vinyl hydroquinone), which indeed showed electro-activity. However oxidation and reduction reversibility was not good, and cycle life was short. This may possibly have been partly due to the fact that when the hydroquinone is oxidized, protons are produced. These accumulate in the battery, and possibly leading to adverse electrochemical effects.[89]

The aim of the research work described was to synthesize and investigate nitrogen analogues of poly(vinylhydroquinone). The idea was based on the fact that p-dimethylamino-N,N-dimethylaniline (62) (a nitrogen anologue of hydroquinone) can be oxidized and reduced electrochemically (fig. 1.9).[90, 91, 92] This compound may be considered to be a model compound for our work. It can be oxidized to a radical cation (63) (the first redox couple) and then to dication (64) (the second redox couple).



(62) (63) (64)

Figure1.9 Redox reactions of p-dimethylamino-N,N-dimethylaniline

In this redox reaction there is no proton produced, so the "proton problem" should not arise. The first redox couple for (62) was reported to be very stable, the second was not.[90, 91, 93]

Chapter II

Synthesis and Characterization of Monomers

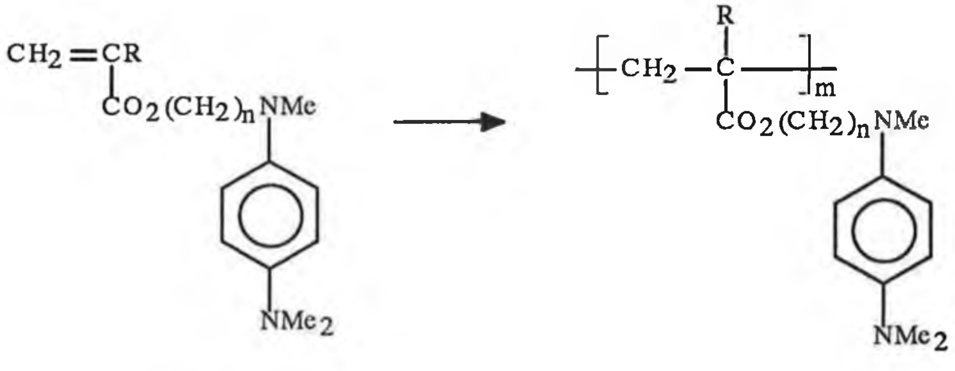
2.1 Introduction

The area of electroactive polymers has been one of the most active research areas in the last two decades. Due to their anticorrosion properties and light weight, the use of electroactive polymers as electrode materials has been explored in a variety of applications. Their use as battery materials[11, 89] and as modified electrodes[6] has been reported.

Our interest in the redox polymers reported in this thesis was based on the expectation that they might have application in areas such as battery manufacture, electrocatalysis etc.

The reason for choosing the p-diaminobenzene system as the electroactive functionality within a polymer is the fact that p-dimethylamino-N,N-dimethylaniline has good electroactive redox properties[90, 93] (section 1.5). There are two ways in which this functional group might be incorporated into a polymer. One is through addition polymerization to produce a polymer with the functional group pendant to the polymer chain. Another way is through condensational polymerisation to yield a polymer with the functional group incorporated within the backbone of the polymer chain. Use of the latter approach may be somewhat limited because of constraints caused by the backbone,[10] and in our work effort was concentrated on the production of polymers with the appropriate group present in a pendant manner.

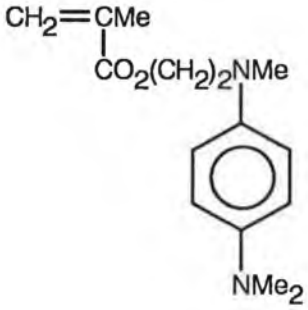
Monomers for addition polymerization commonly have a carbon-carbon double bond where polymerization can be initiated by an appropriate ionic or free radical initiator. We therefore required appropriate vinylic monomers in which the redox active functional group was connected to an alkene unit. We chose to synthesize acrylate derivatives because of their general ease of polymerization. The target vinyl monomers (66) and polymers (67) were of the type:



(66) (67)

The presence or absence of alkyl substitution (R = H, polyacrylates; R = Me, polymethacrylates) on the polymer backbone might potentially influence the redox behaviour of the pendant group due to conformational and/or steric effects. Also, the separation between the redox active unit and the polymer backbone might influence the redox behaviour. Both of these factors could be studied in the series of polymers selected for investigation.

The synthesis and characterization of these monomers (68, 69, and 70) will be discussed in this chapter.



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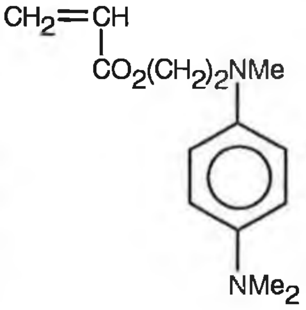

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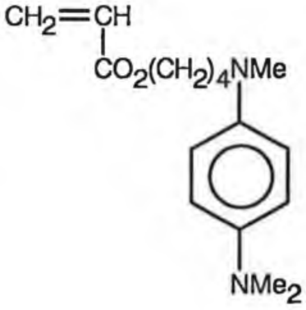
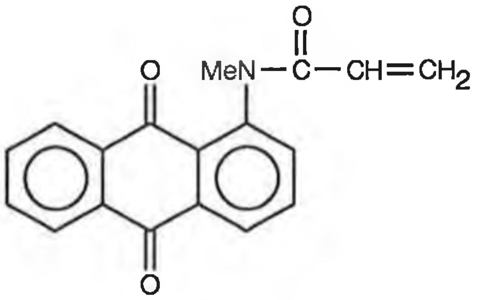


(70)

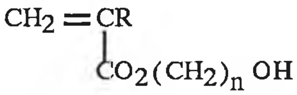
The synthesis of monomer (71) with anthraquinone group will be disscussed as well.



(71)

2.2 General synthetic approach

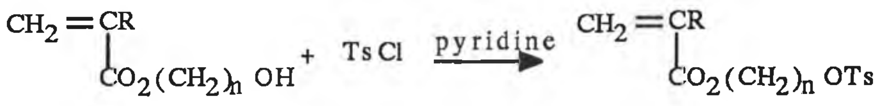
The commercial availability of the hydroxyalkyl acrylates and methacrylates (72), (73) and (74) suggested these as appropriate precursors to the required N,N,N',N'-tetraalkyl-p-diaminobenzenes.



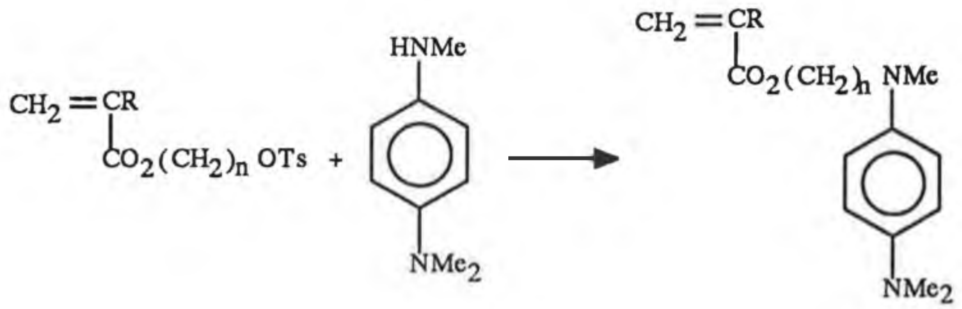
$$CH_2{=}CR\text{—}CO_2(CH_2)_nOH$$

(72) R = Me, n = 2; (73) R = H, n = 2; (74) R = H, n = 4

Replacement of the primary alcohol groups by the appropriate arylamino function would then yield the required monomers, involving a substitution process. The general scheme to be adopted for the synthesis of the monomers is shown in figure 2.1.



$$CH_2{=}CR\text{—}CO_2(CH_2)_nOH + TsCl \xrightarrow{\text{pyridine}} CH_2{=}CR\text{—}CO_2(CH_2)_nOTs$$

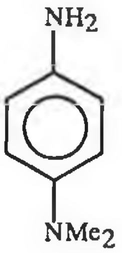


$\left[\begin{array}{l} Ts = 4\text{-}MeC_6H_4SO_2 \\ R = Me, H;\ n = 2, 4 \end{array}\right]$

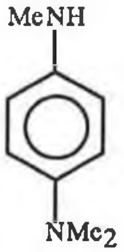
Figure 2.1 Reaction scheme for the synthesis of the required monomers

In order to introduce the required arylamino functional group into a polymer chain, compound (77), p-dimethylamino-N-methylaniline was required. This compound was not commercially available, though p-diaminobenzene (75) and p-dimethylaminoaniline (76) could be purchased. It was therefore necessary to have available an efficient method for the monomethylation of an aromatic amino group.

(75)



(76)

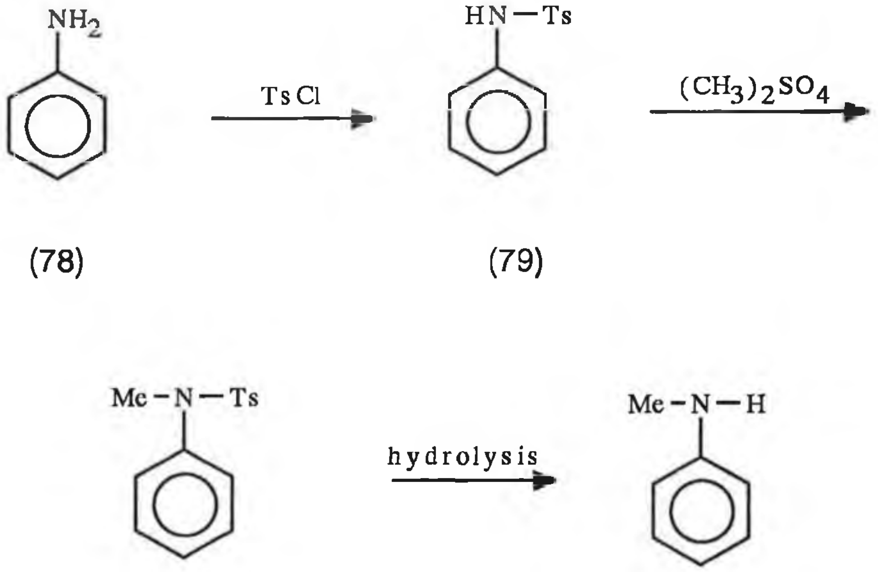


(77)

In the following subsection the application of a monomethylation process to the formation of (77) is discussed. It has also been extended as a general reaction for the monomethylation of other primary aromatic diamines. Thus N,N'-dimethyl-p-diaminobenzene (87) and N,N'-dimethyl-o-diaminobenzene (91) have been synthesized from p-diaminobenzene (75) and o-diaminobenzene (89) respectively and the process has been also applied to the synthesis of 1-methylamino-9,10- anthraquinone (96).

2.3 Monomethylation of amines

There are several methods available for monomethylation of primary aromatic amines. The most commonly used one is a three-stage synthesis starting from an aromatic amine (78) via the p-toluenesulphonyl derivative (79) and methylation with dimethyl sulphate, followed by hydrolysis of the N-methyl-p-toluenesulphonyl intermediate (80).[94-97] This method was found to involve drastic reaction conditions to be time consuming[98] (see fig. 2.2).

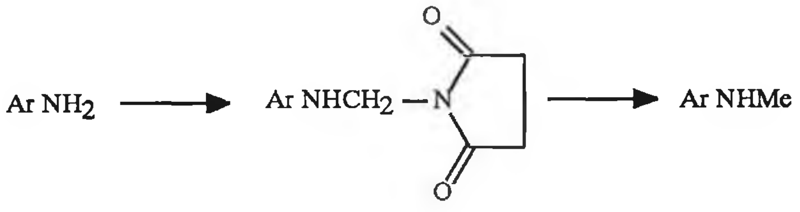


(78) (79) (80) (81)

Figure 2.2 A three stage procedure for monomethylation of aniline

Other methods, for example, direct or Eschweiler-Clarke alkylation, is complicated by the formation of tertiary amines.[99]

For the present purposes a two-stage synthesis from a primary aromatic amine (78) involving conversion to the N-arylaminomethyl succinimide (82), followed by reduction with sodium borohydride to give the N-methylated amine (83), seemed attractive.



(78) (82) (83)

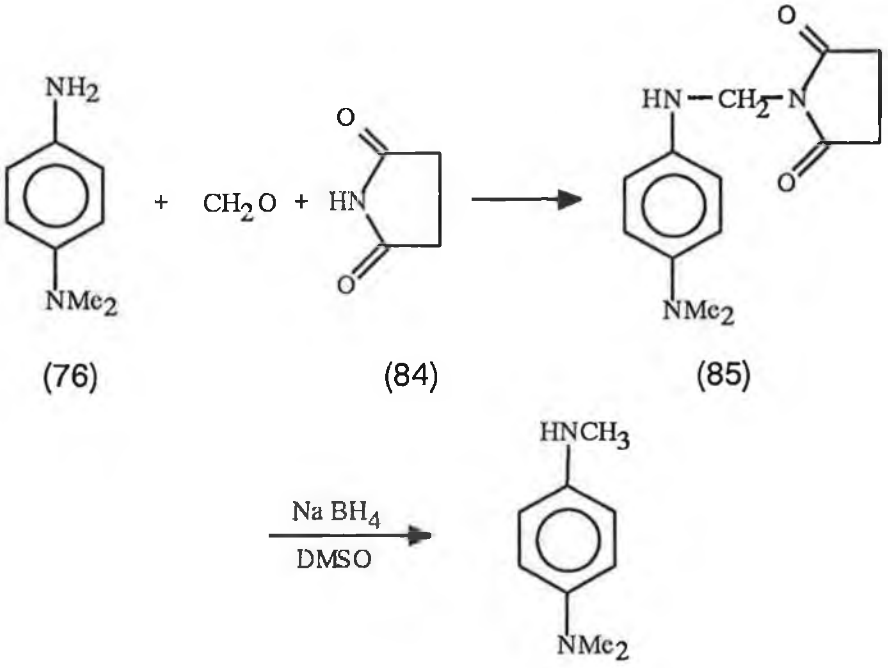
The reaction of aromatic amines (78) with aqueous formaldehyde and succinimide in ethanol was first reported in 1962 to provide good yields of N-arylaminomethyl succinimides (82).[100]

Sodium borohydride has long been used as a mild and selective reducting agent.[101-102] In 1968 its use for reductive ring opening of cyclic imides was reported[103]. In 1973 it was reported that treatment of N-arylaminomethyl succinimides with sodium borohydride in dimethyl sulfoxide resulted in an exothermic reaction to give the corresponding N-methyl aromatic amines, and the process was applied to anilines with halo, alkyl, cyano, carboethoxy, alkyloxy, alkylthio, and amido substituents, as well as to aminopyridines and naphthylamine[104], though the effect of additioned amino substituents was not investigated.

In the present work the above sequence has been applied to the monomethylation of p-dimethylaminoaniline(76), p-diaminobenzene (75) and o-diaminobenzene (89) . It was also applied to the monomethylation of 1-amino-9,10-anthraquinone (94).

2.4 Results and discussion

2.4.1 Synthesis of P-dimethylamino-N-methylaniline (77)



(76) (84) (85)

(77)

Addition of aqueous formaldehyde to an ethanolic solution containing p-dimethyaminoaniline (76) and succinimide (84) yielded p-dimethylamino-N-succinimidomethylaniline (85) whose structure was supported by spectroscopy and elemental microanalysis.

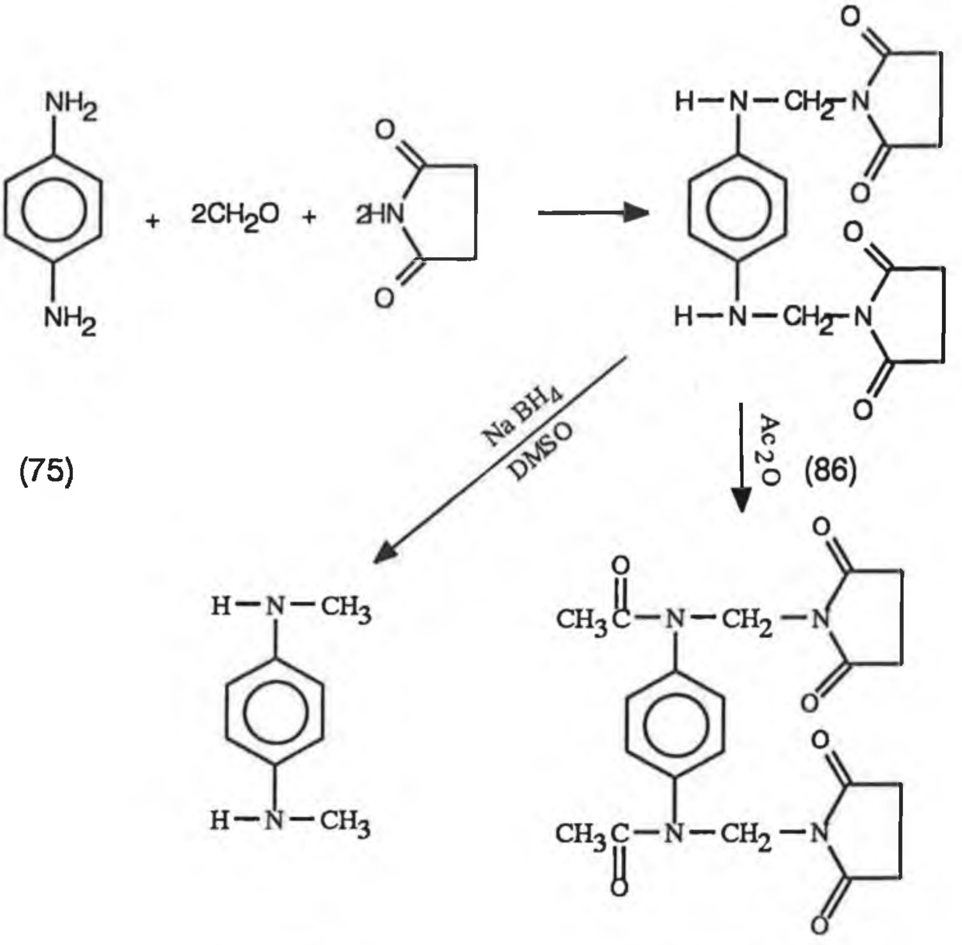
The ^{1}H-NMR spectrum of (85) showed a singlet at 2.60ppm for the four methylene protons in the succinimide ring, a singlet at 2.79ppm for the six methyl protons, a broad peak at 4.50ppm for the NH proton (disappeared on addition of D_2O), a doublet at 4.92ppm for the two N-methylene protons, and a multiplet at 6.65-6.75 for the four aromatic protons, consistent with the assigned structure.. The ^{13}C-NMR spectrum confirmed this structure. The peak at 28.03ppm was assigned to the succinimidomethylenes, the one at 41.72ppm to the two methyl groups and that at 49.72ppm to the N-methylene group. Those at 115.17 and 115.31ppm were assigned to the aromatic methine groups, those at 136.01 and 145.06ppm to the aromatic quaternary carbons and that at 177.51ppm to the carbonyl carbons.

Reduction of compound (85) by sodium borohydride in DMSO yielded p-dimethylamino-N-methylaniline (77)[105], confirmed by spectroscopy and elemental analysis. In the ^{1}H-NMR spectrum, one N-methyl group appeared as a three proton singlet at 2.64ppm, the two identical N-methyls appeared as a six proton singlet at 2.74ppm, the NH group appeared as a singlet at 3.33ppm (disappeared on addition of D_2O), and the four aromatic protons appeared as two doublets at 6.49 and 6.69ppm. In the ^{13}C-NMR spectrum the HNMe methyl carbon appeared at 31.17ppm, the two identical NMe_2 methyl appeared at 41.86, the aromatic methine carbons appeared at 113.36 and 115.57ppm, and the aromatic quaternary carbons appeared at 141.83 and 143.47ppm. Compound (77) has been made using the method shown in figure 2.2.[98,105]

2.4.2 Methylation of p-diaminobenzene

Having successfully applied the process to the monomethylation of (76), it was of interest to investigate its use in the methylation of some other diaminobenzenes.

Reaction of p-diaminobenzene (75) with formaldehyde and succinimide gave the corresponding bissuccinimidomethyl derivative (86), which may be used without further purification in the reduction step.



(75) (86) (87) (88)

Due to the insolubility of compound (86) in most common solvents, it was acetylated to facilitate further purification and characterization. Acetylation was achieved by heating the compound in acetic anhydride at 100°C.

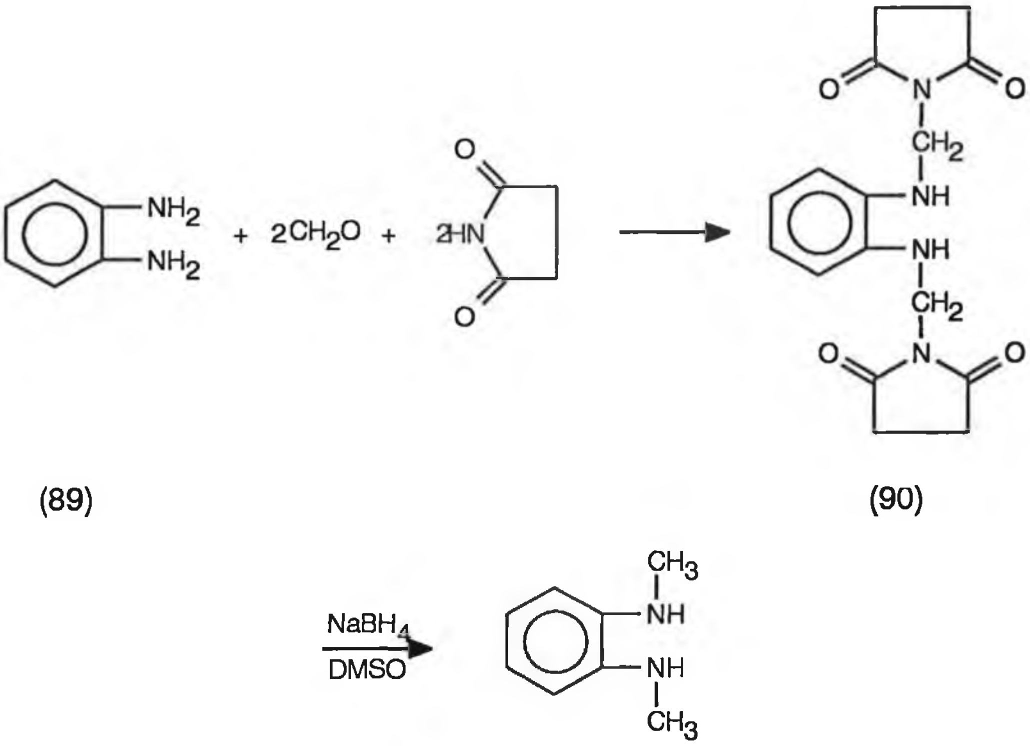
The infrared, ^{1}H-NMR and ^{13}C-NMR spectra and elemental analysis of the diacetyl derivative (88) were obtained after recrystallization from acetonitrile. and all were consistent with the assigned structure. Thus in the ^{1}H-NMR spectrum, the acetyl methyl groups appeared as a six proton singlet at 1.83ppm, the methylene groups in the two succinimide rings appeared as an eight proton singlet at 2.51ppm, the N-methylene groups appeared as a four proton singlet at 5.35ppm and the four aromatic protons were identical, appearing at 7.17ppm as a singlet. In the ^{13}C-NMR spectrum, the peak at 21.65ppm was assigned to the methyls in the acetyl groups , the peak at

27.41ppm to the four methylene carbons in the succinimide rings, and the peak at 48.73ppm to the two N-methylene carbons. There were four other resonances in the spectrum, at 129.84ppm for the aromatic methine carbon, at 139.84ppm for the aromatic quaternary carbons, at 169.07ppm for the acetyl carbonyls, and at 176.48ppm for the succinimide carbonyls. The assignment for the two kinds of carbonyls was supported by comparison with the ^{13}C-NMR spectrum of p-dimethylamino-N-succinimidomethylaniline (85), in which the succinimide carbonyl carbons appeared at 177.51ppm.

The N,N'-bis(succinimidomethyl)-p-diaminobenzene (86) was reduced by sodium borohydride in DMSO to give N,N'-dimethyl-p-diaminobenzene (87). Compound (87) has been synthesized using the method shown in figure 2.2.[98,106] The ^{1}H-NMR spectroscopy clearly confirmed the structure as (87), displaying a six proton singlet at 2.74ppm (methyls), a two proton singlet at 3.22ppm (NH; disappeared on addition of D_2O), and a four proton singlet at 6.53ppm (aromatic).

2.4.3 Synthesis and characterisation of N,N'-dimethyl-o-diaminobenzene

Reaction of o-diaminobenzene (89) with succinimide and formaldehyde gives N,N'-bis(succinimidomethyl)-o-diaminobenzene (90) which may be used without further purification in the reduction step .



(89) (90) (91)

The infrared, ^{1}H-NMR and ^{13}C-NMR spectra and elemental analysis of the bissuccinimidomethyl derivative (90) were obtained after recrystallization from chloroform and all were consistent with the assigned structure. Thus, in the ^{1}H-NMR spectrum, the methylene groups in the succinimide ring appeared as a eight proton singlet at 2.62ppm, the NH group appeared as a two proton triplet at 4.62ppm (disappeared on addition of D_2O), the N-methylene groups appeared as a four proton doublet at 4.95ppm, and the four aromatic protons appeared as a broad singlet at 6.80ppm.

The ^{13}C-NMR spectrum and the off-resonance spectrum also clearly supported the structure of N, N'-bis(succinimidomethyl)-o-diaminobenzene (90). The assignment of the ^{13}C-NMR spectrum with help of the off-resonance spectrum was tabulated in table 2.1.

Table 2.1 Assignments of ^{13}C-NMR spectrum for N,N'-bis(succinimidomethyl)-o-diaminobenzene (90)

^{13}C-NMR (ppm)	off-resonance	types of carbons	assignments
28.13	triplet	secondary	CH_2s in succinimidyl rings
49.20	triplet	secondary	N-CH_2
116.27	doublet	tertiary	aromatic CHs meta to N
121.58	doublet	tertiary	aromatic CHs ortho to N
134.36	singlet	quaternary	aromatic quaternary carbons
177.64	singlet	quaternary	carbonyls in succinimidyl group

N,N'-Bis(succinimidomethyl)-o-diaminobenzene (90) was reduced to N,N'-dimethyl-o-diaminobenzene (91) by sodium borohydride in DMSO. Compound (90) has been synthesized using the method shown in figure 2.2.[98, 106] The ^{1}H-NMR spectroscopy clearly confirmed the structure as that of N,N'-dimethyl-o-diaminobenzene (91), displaying a six proton singlet at 2.74ppm (methyls), a two proton singlet at 3.21ppm (NH; disappeared on addition of D_2O), and two multiplets at 6.60 and 6.80ppm (four aromatic protons).

2.4.4 Attempted methylation of m-diaminobenzene

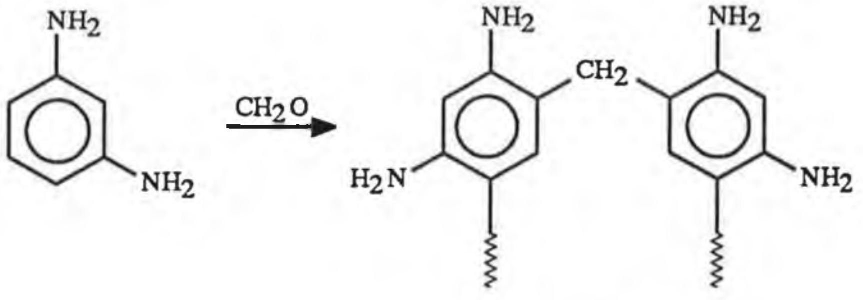
Methylation of m-diaminobenzene (92) was also attempted.

A yellow precipitate formed when aqueous formaldehyde was added to an ethanol solution of m-diaminobenzene (92) and succinimide. Comparison of the IR spectrum of this product with that of p- and o-diaminobenzene succinimidomethyl derivatives (86) and (90), showed that the strong imide carbonyl absorption peaks appearing at approximately 1688 cm^{-1} in the spectra of these succinimido derivatives were absent from the spectrum of this yellow substance. Also the peak at 3361cm^{-1} in the spectrum of this yellow substance was much broader than in those of the other two compounds.

Addition of aqueous formaldehyde to an ethanol solution of m-diaminobenzene (92) in the absence of succinimide gave a similar yellow powder. The infrared spectrum showed that this yellow powder was identical to the one obtained in the presence of succinimide. This experiment proved that succinimide was not involved in the reaction with m-diaminobenzene to form the yellow powder. It was also recovered unchanged after three hours reduction with sodium borohydride at 100^{o}C. Because this yellow substance is only soluble in DMSO at 100^{o}C, further purification was impossible. Acetylation was attempted, but without success.

It has been reported that Mannich reactions of N,N-dialkylarylamines under classical conditions occur at the para-position if that position is unsubstituted[107]. Also Mannich reactions of secondary arylamines to give products from attack at nitrogen as well as ring-substitution products involving attack at the para-position have been reported.[108,109]

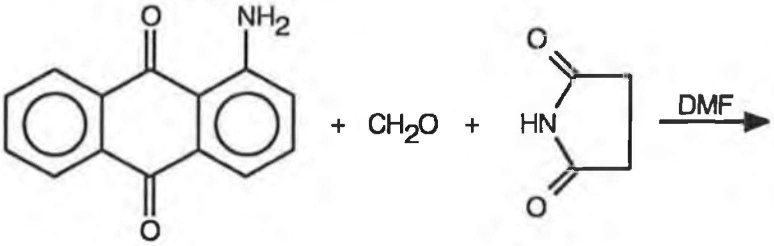
Amino groups are strongly activating and ortho-, para-directing in electrophilic aromatic substitution reactions. In m-diaminobenzene (92), positions 2, 4 and 6 are highly activated by both amino groups, possibly make them more active than amino groups. Mannich reaction involving attack by formaldehyde at these positions could give a polymer such as (93). For p-diaminobenzene (75), and o-diaminobenzene (89) there is no such doubly activated position and reaction with formaldehyde occurs at the amino groups.



(92) (93)

2.4.5 Methylation of 1-aminoanthraquinone (94)

The amino group is electron donating, and its presence on an anthraquinone group will modify the normal redox behaviour of the anthraquinone. It was of interest to incorporate an aminoanthraquinone into a polymer. 1-methylamino-9,10-anthraquinone (96) was prepared for this purpose.



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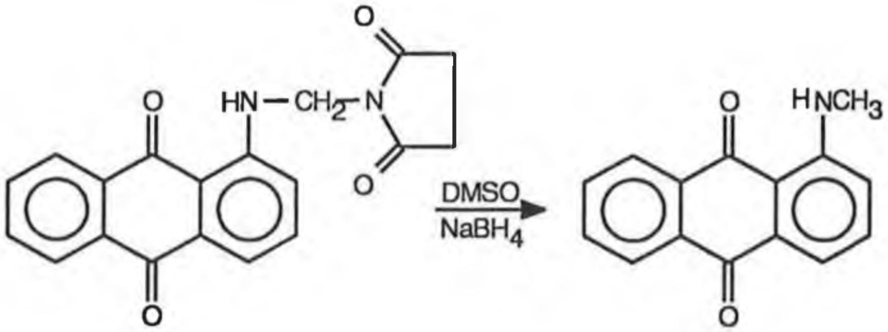
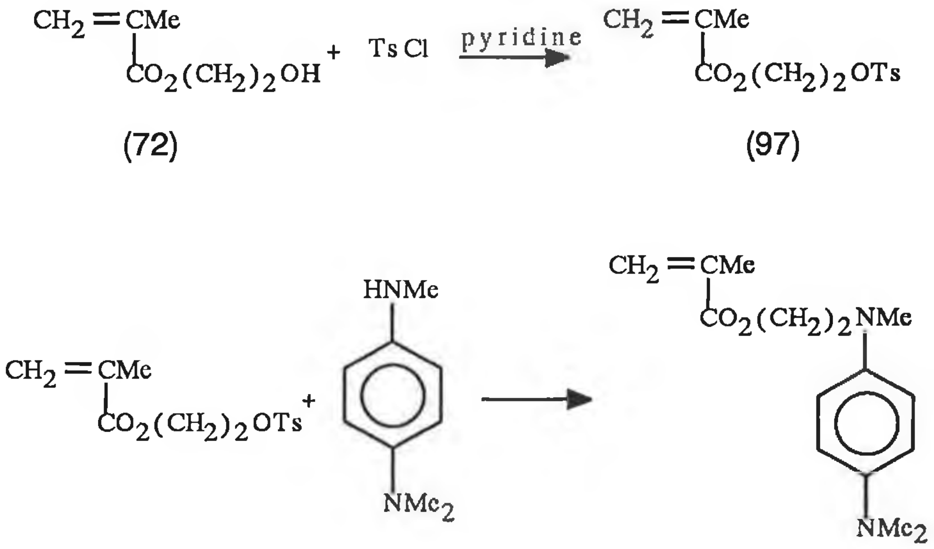


(95) (96)

The solubility of 1-amino-9,10-anthraquinone (94) in ethanol was poor, so dimethylformamide (DMF) was used as solvent. Addition of aqueous formaldehyde to a solution of 1-amino-9,10-anthraquinone (94) and succinimide in dimetyl formamide yielded an orange precipitate which could be used directly in the reduction step. Because this intermediate compound (95) was extremely insoluble. Characterization was impossible. In the reduction reaction, although at the beginning the orange solid did not dissolve in dimethylsulfoxide at 100°C, once sodium borohydride was added, the solid rapidly disappeared and 1-methylamino-9,10-anthraquinone[110] (96) was formed. Its structure was confirmed by spectroscopy and elemental analysis. In the IR spectrum, the NH stretch was seen at 3303cm^{-1} and a peak at 1672cm^{-1} indicated the presence of carbonyl in the structure. In the ^{1}H-NMR spectrum, a singlet at 3.05ppm showed the presence of an N-methyl group, a broad singlet at 9.65ppm, which disappeared when D_2O was added, confirmed the presence of one NH proton. The aromatic region from 6.9 - 8.4ppm was very complicated. COSY was used to assign the peaks in this range. Also, the coupling constants were very helpful in the assignment of peaks in the aromatic range. A doublet at 7.05ppm was assigned to the proton at position 2, and a triplet at 7.57 to the proton at position 3. Coupling between the protons at position 2 and 3 was observed in the COSY spectrum. A doublet at 7.61ppm was assigned to the proton at position 4. Two triplets at 7.71 and 7.77ppm were assigned to the protons at positions 7 and 6 respectively. The two doublets at 8.24 and 8.27ppm were assigned to the protons at positions 8 and 5. The COSY spectrum showed the coupling of the group of peaks around 7.74ppm and the group of peaks around 8.25ppm. The ^{13}C-NMR spectrum showed a methyl group at 29.57ppm, two carbonyl carbons at 183.78 and 184.90ppm, and one aromatic N-substituted quaternary carbon at 152.46ppm. The remaining 11 aromatic carbons appeared between 112.98 and 135.28ppm.

2.4.6 Synthesis and characterization of 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98)

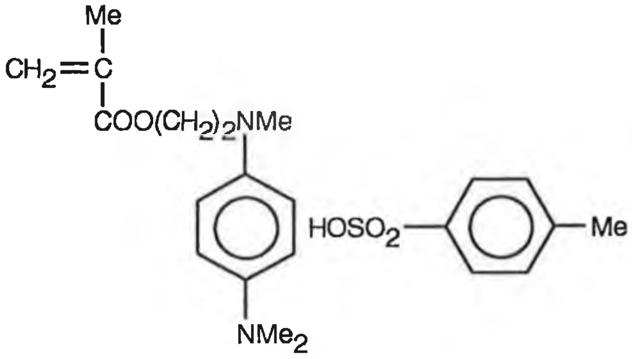


(72) (97)

(77) (98)

2-Hydroxyethyl methacrylate (72) was treated with p-toluenesulphonyl chloride in pyridine to give the corresponding tosylate (97) as a liquid. IR spectroscopy confirmed the disappearance of the hydroxyl group (disappearance of the broad OH stretch at 3400cm^{-1} present in the spectrum of 2-hydroxyethyl methacrylate). TLC showed one spot which was different from the starting materials. The ^{1}H-NMR spectrum of the product was consistent with it being the tosylate (97) (see experimental section), and it was used directly in the next step of the synthesis without further purification.

Reaction of tosylate (97) with p-dimethylamino-N-methylaniline(77) gave the required monomer (98). 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98) was a liquid , and in liquid form underwent ready oxidation by air. Since the purity of monomers is critical for successful polymerizations, it was decided to use a suitable salt of the monomer to make it easier to isolate and purify in the solid state. The monomer (98) formed a crystalline salt (99) with p-toluene sulphonic acid. The salt (99) was characterized after four recrystallizations from toluene, and was found to be formed in a 1:1 ratio, that is one monomer molecule combined with one acid molecule, by both microanalysis and integration of the ^{1}H-NMR spectrum.



(99)

Both ^{1}H-NMR and ^{13}C-NMR confirmed the composition of the monomer.

The assignment of the ^{1}H-NMR spectrum was as follows: a three-proton singlet at 1.87ppm was assigned to the methyl attached to the carbon-carbon double bond (confirmed from the ^{1}H-NMR spectrum of the free monomer), and a singlet at 2.34ppm to the methyl of the toluene sulphonic acid. Broad peaks at 2.98 (3H) and 3.14ppm (6H) were assigned to the three N-methyl groups. A methylene connected to carboxyl group is expected to be more deshielded than a methylene connected to a nitrogen, so the two-proton peak at 3.63ppm was assigned to the N-methylene, and the two-proton peak at 4.27 to the O-methylene. Two peaks at 5.54 (1H) and 6.02ppm (1H) were assigned to the two protons on the carbon-carbon double bond, two broad peaks at 6.72 and 7.43ppm to the four aromatic protons in the diaminobenzene ring, two doublets at 7.17 and 7.81ppm to the four aromatic protons in the p-toluene sulphonic acid unit. Comparision of the integrations of the two methyl groups at 1.87 (from monomer) and 2.34 (from acid)ppm showed the ratio of monomer and acid was 1:1.

Table 2.2 ^{13}C-NMR spectral data for the p-toluene sulphonic acid salt (99) of 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98)

^{13}C-NMR (ppm)	DEPT-135	Types of carbon	Assignment
18.19	positive	CH_3	MeC=C
21.26	positive	CH_3	MeC_6H_4*
39.10	positive	CH_3	MeN
46.86	positive	CH_3	MeN
51.05	negative	CH_2	CH_2 -N
61.35	negative	CH_2	CH_2 -O
112.90	positive	CH	aromatic CH in diaminobenzene ring
120.89	positive	CH	aromatic CH in diaminobenzene ring
125.93	positive	CH	aromatic CH in toluene sulphonic acid ring*
126.07	negative	CH_2	CH_2 =C
128.81	positive	CH	aromatic CH in toluene sulphonic acid*
132.28	none	C	aromatic C in toluene sulphonic acid *
135.77	none	C	quaternary carbon in the vinyl group
140.03	none	C	aromatic C in diaminobenzene ring
142.30	none	C	aromatic C in diaminobenzene ring
148.00	none	C	aromatic C in toluene sulphonic acid*
167.15	none	C	carbonyl

* Correspond to peaks in the ^{13}C-NMR spectrum of p-toluenesulphonic acid

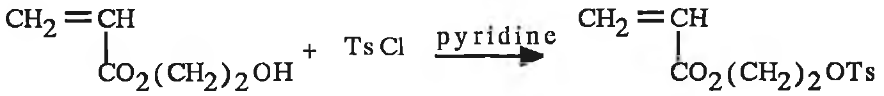
The ^{13}C-NMR spectrum was also consistent with the salt (99). The observed peaks, also those observed in the DEPT-135 spectrum are listed in table 2.2.

This assignment was supported by the ^{13}C-NMR spectra of both p-toluene sulphonic acid and of the polymer derived from this monomer.

For use in polymerization, the monomer (98) was liberated from the salt (99) by addition of aqueous sodium hydroxide. It could then be extracted into an organic solvent for subsequent use.

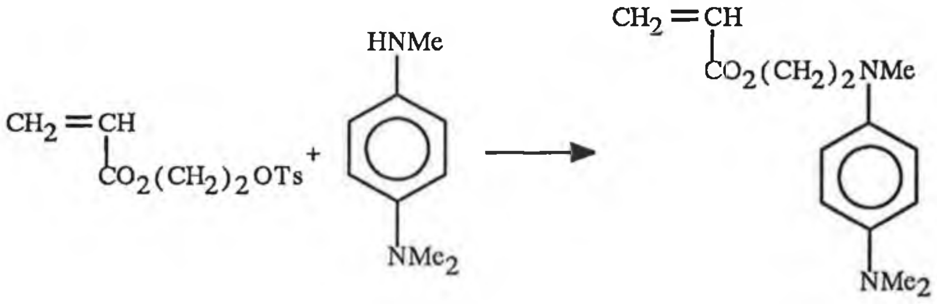
2.4.7 Synthesis and characterisation of monomer 2-(p-dimethylamino-N-methylanilino)ethyl acrylate (101)

The reaction sequence used for the synthesis of this monomer was analogous to that used for 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98) in the previous section .



$$CH_2{=}CH{-}CO_2(CH_2)_2OH + TsCl \xrightarrow{pyridine} CH_2{=}CH{-}CO_2(CH_2)_2OTs$$

(73) (100)

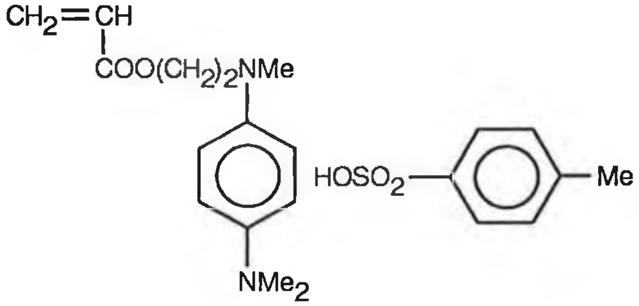


(77) (101)

2-Hydroxyethyl acrylate (73) was used as the starting material. It reacted readily with p-toluene sulphonyl chloride to give tosylate (100). IR confirmed the disappearance of the hydroxyl group (disappearance of the OH stretch at 3400 cm^{-1} present in 2-hydroxyethyl acrylate). The ^{1}H-NMR spectrum of the tosylate (100) is consistent with the structure. It was used directly in the next step of synthesis without further purification.

Reaction of tosylate (100) with p-dimethylamino-N-methylaniline (77) gave the required monomer 2-(p-dimethylamino-N-methylanilino)ethyl acrylate (101).

This monomer was also a liquid, so it was isolated and purified as the 1:1 salt with para-toluene sulphonic acid (102).



(102)

In the ^{1}H-NMR spectrum, the singlet at 2.34ppm was assigned to the methyl group on the toluene sulphonic acid, the two broad singlets at 2.97 and 3.15ppm to three N-methyl groups, the broad singlet at 3.63 to N-methylene, and the broad singlet at 4.27ppm to O-methylene group.

The group of peaks from 5.5 to 6.5ppm were assigned to the three vinylic protons. Their coupling constants allowed them to be precisely assigned.

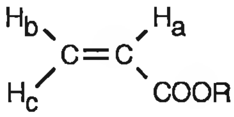


Figure 2.3 Proton coupling in a vinyl group

From the two coupling constants obtained, 10.52 and 17.22Hz, it was easy to tell that the doublet centred at 5.81ppm (J=10.52Hz) was H_b, the double doublet centred at 6.06ppm (J=17.22, 10.52Hz)was H_a, the doublet at 6.33ppm(J=17.22Hz) was H_c. Because in an olefinic system, within a single molecule, J_{trans} is normally larger than J_{cis}. Thus with J_{trans} = 17.22Hz and Jcis = 10.52Hz, the above assignments are established.

The two broad peaks at 6.18 and 7.43ppm were assigned to the four aromatic protons from the diaminobenzene, the two doublets at 7.18 and 7.81ppm to the four aromatic protons in the toluene sulphonic acid. The integration of this spectrum showed that the ratio of this salt was 1:1.

Table 2.3 Assignment of the ^{13}C-NMR spectrum for salt (102).

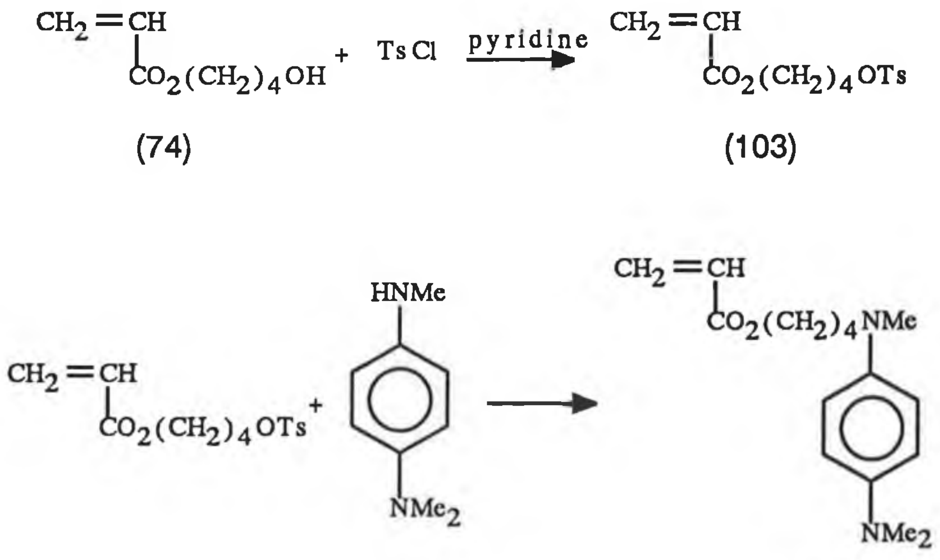
^{13}C-NMR (ppm)	DEPT-135	Types of carbon	assignment
21.26	positive	CH_3	in the toluene group*
39.16	positive	CH_3	N-Me
46.81	positive	CH_3	N-Me
51.10	negative	CH_2	CH_2-N
61.09	negative	CH_2	CH_2-O
112.99	positive	CH	aromatic CH in diaminobenzene ring
120.82	positive	CH	aromatic CH in diaminobenzene ring
125.93	positive	CH	aromatic CH in toluene sulphonic acid ring*
127.89	positive	CH	CH in vinyl group
128.82	positive	CH	aromatic CH in toluene sulphonic acid ring*
131.33	negative	CH_2	CH_2 in vinyl group
132.28	none	C	aromatic C in toluene sulphonic acid ring*
140.05	none	C	aromatic C in diaminobenzene ring
142.29	none	C	aromatic C in diaminobenzene ring
148.00	none	C	aromatic C in toluene sulphonic acid ring*
165.89	none	C	carbonyl

* Correspond to peaks in the ^{13}C-NMR of p-toluenesulphonic acid

The ^{13}C-NMR spectrum is also consistent with the salt structure(102). The assignment of the ^{13}C-NMR spectrum with the support of DEPT-135 spectrum is tabulated in table 2.3. This assignment was supported by comparision of this spectrum with that of the other two monomers in section 2.4.6 and section 2.4.8 also by the comparision with the polymer spectrum in next chapter and the spectrum of p-toluene sulphonic acid.

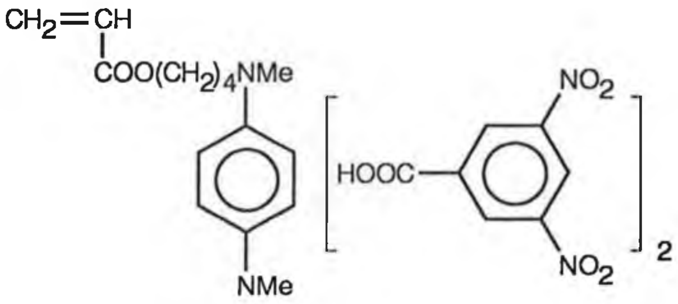
2.4.8 Synthesis and characterisation of 4-(p-dimethylamino-N-methylanilino)butyl acrylate (104).

The reaction scheme was similar to that used for the previous two monomers.



(77) (104)

4-Hydroxybutyl acrylate (74) tosylated easily. It was used directly in the reaction with p-dimethylamino-N-methylaniline (77) to give compound (104). The salt of this monomer with p-toluene sulphonic acid did not crystallize, so the preparation of alternative salts was investigated. The salt (105) with 3,5-dinitrobenzoic acid was a yellow powder and was characterized after three recrystallisations from toluene-chloroform. This salt (105) was a 1:2 salt, that is one monomer molecule combined with two 3,5-dinitrobenzoic acid molecules, as proved by the microanalysis and ^{1}H-NMR spectrum integration.



(105)

In the ^{1}H-NMR spectrum, the two methylene groups between the O-methylene and N-methylene groups appeared as a four proton singlet at 1.70ppm, the O-methylene group appeared as a two proton singlet at 4.15ppm, the N-methylene appeared as a two proton singlet at 3.44ppm. The three N-methyl groups appeared as a nine proton peak at 3.12ppm. The doublet (J = 10.26 Hz) at 5.81ppm was assigned to H_b (see fig. 2.3), the double doublet (J =10.26 Hz, J = 16.86 Hz) at 6.02 - 6.13ppm was assigned to H_a, the doublet(J = 16.86 Hz) at 6.37ppm was assigned to H_c. The broad peak at 7.08ppm was assigned to the four aromatic protons from the diaminobenzene. The triplet (J = 2.20 Hz) at 9.15ppm was assigned to the aromatic proton para to the carboxylic acid group. The doublet (J = 2.20 Hz) at 9.20ppm was assigned to the aromatic protons ortho to the carboxylic acid group. The broad peak at 9.39ppm was assigned to the carboxylic acid proton (disappeared on addition of D_2O). The integrations of the peaks showed that one monomer molecule combined with two 3, 5-dinitrobenzoic acid molecules.

^{13}C-NMR spectroscopy is consistent with the assigned structure. and it is tabulated in table 2.4.

Table 2.4 Assignment of ^{13}C-NMR spectrum for the 3,5-dinitrobenzoic acid salt (105) of 4-(p-dimethylamino-N-methylanilino)butyl acrylate

^{13}C-NMR (ppm)	DEPT-135	types of carbons	assignment
22.39	negative	secondary	CH_2 connected with CH_2N
25.80	negative	secondary	CH_2 connected with CH_2O
41.78	positive	primary	NMe
43.51	positive	primary	NMe
55.31	negative	secondary	CH_2-N
63.62	negative	secondary	CH_2-O
117.00	positive	tertiary	aromatic CH in diaminobenzene ring
121.03	positive	tertiary	aromatic CH in the acid ring*
128.12	positive	tertiary	CH in vinyl group
129.54	positive	tertiary	aromatic CH in the acid ring*
130.92	negative	secondary	CH_2 in vinyl group
137.86	none	quaternary	aromatic C in the acid*
139.10	none	quaternary	aromatic C in diaminobenzene ring
140.50	none	quaternary	aromatic C in diaminobenzene ring
148.29	none	quaternary	aromatic C in the acid*
166.11	none	quaternary	carbonyl*
166.41	none	quaternary	carbonyl

* Correspond to peaks in the ^{13}C-NMR of 3, 5-dinitrobenzoic acid

2.4.9 Line broadening in the NMR spectra of the diaminobenzene type monomers

In the ^{1}H-NMR spectra of the monomer salts (99) (102) (105), some of the peaks are broad. The cause of the line broadening in these samples were studied.

There are a number of possible for line broadening in an NMR spectrum.[111] The three major cases in which the line broadening is not due solely to the spectrometer are:

(a) intermediate rates of exchange between two interconverting species[111]

(b)the presence of quadrupolar nuclei (in particular ^{14}N)[112]

(c)the presence of paramagnetic species[112] in the sample

For case (a), we should consider a molecule which is interconverting between two states A and B, or a nucleus exchanging between two molecules A and B

$$A \rightleftharpoons B$$

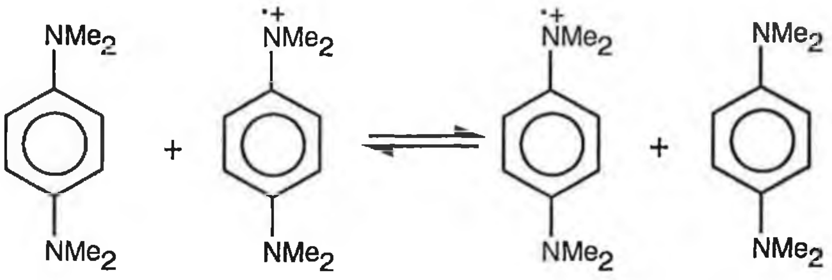
If the rate of interconversion of A and B is slow (on the NMR time scale), then we will observe the NMR spectra of the two separate species A and B. If the rate of interconversion is fast, the NMR spectrum observed is one "averaged" spectrum in which the chemical shifts and coupling are the averages of the values in A and B. When the rate of exchange is intermediate, broad lines in the NMR spectrum will be observed.[111]

For case (b), line broadening is caused by the quadrupolar moment. Nuclei with spin numbers $I = 1/2$ have a spherically symmetric charge distribution whereas higher spin numbers are associated with charge distributions of lower symmetry, so that nuclei with $I > 1/2$ (such as ^{14}N, ^{2}H, ^{35}Cl, ^{71}Br) mostly possess an electric quadrupolar moment.[113]

The quadrupolar moment gives rise to an electric field gradient at the nuclei, providing a highly efficient relaxation mechanism, both for themselves and for any directly connected neighbouring nuclei. Therefore the observed absorption lines associated with these nuclei are correspondingly broad.[113]

Case (c) is termed paramagnetic broadening and results from the presence of paramagnetic molecules or ions in the sample under investigation. The electron magnetic moment is some 10^3 times larger than nuclear magnetic moments. Consequently the motions of paramagnetic lattices will produce very intense fluctuating magnetic fields and greatly reduce relaxation times. Under these conditions, the nuclear magnetic resonance lines of paramagnetic substances are usually very broad.[114] Furthermore, the presence of even small quantities of paramagnetic impurities in a sample can cause line-broadening.[114]

Peak broadening phenomena in the NMR spectra of p-dimethylamino-N,N-dimethylaniline have been known for some time and their origins have been investigated.[115-117] Generally it is agreed that the peak broadening is caused by the electron exchange reaction between neutral p-dimethylamino-N,N-dimethylaniline (62) and its one electron oxidation product (63). The neutral molecule (62) is diamagnetic, while the free radical cation (63) is paramagnetic. The exchange reaction can be written as follows:



(62) (63) (63) (62)

In 1956, it was first shown by Bruce that the cause of the NMR peak broadening was this electron exchange reaction,[115] and the electron exchange reaction rate was measured using the following relationship:

$$k = \pi\Delta\nu / (3^{1/2}A) \qquad 2.1$$

where k is the reaction transfer rate constant, $\Delta\nu$ is the full width in frequency at half-maximum intensity of the resonance line, and A is the molar concentration of free radical. In the Bruce's experiment, Wurster's blue as the acetic acid salt, the product derived from p-dimethylamino-N,N-dimethylaniline by one electron oxidation, was added into neutral P-dimethylamino-N,N-dimethylaniline in different concentrations. The magnitude of the broadening was the same for both types of proton (aromatic and methyl) and it increased linearly with the concentration of Wurster's blue. The lines for the two other types of proton, those of water and acetate ion present in the solution, remained narrow for all concentrations of Wurster's blue used in the experiment. It was therefore concluded that the broadening of the p-dimethylamino-N,N-dimethylaniline lines was due to electron exchange only and not to thermal paramagnetic relaxation. This work was done using deuterium oxide as solvent.

In 1963, further investigation of this electron exchange reaction was carried out in an aprotic solvent (acetonitrile).[116] Similar results were obtained, and it was noted that in solution p-dimethylamino-N,N-dimethylaniline could be oxidized by air resulting in the generation of micromolar concentrations of the cation radical which could lead to peak broadening in the NMR spectrum.

In the ^{1}H-NMR spectra of monomer salts (99) (102) (105), the broadening of some of the peaks was observed. Other peaks remained sharp over a wide temperature range. Taking 3,5-dinitrobenzoic acid salt (105) of 4-(p-dimethylamino-N-methylanilino)butyl acrylate as an example, the spectra at different temperature of (105) are shown in figure 2.4. The sample was firstly heated to 55^{o}C, then cooled down. The spectra in figure 2.4 were recorded during cooling.

In the spectra in figure 2.4, some peaks remain essentially unchanged as temperature varies, some changed dramatically as temperature is varied.

These peaks are tabulated in table 2.5 as two groups based on the spectrum at 20°C in this figure. Group A is the peaks essentially unchanged. Group B is the peaks changed dramatically as temperature is varied.

Table 2.5 Line broadening in figure 2.4

GroupA: peaks unchanged		GroupB: peaks with dramatic change	
peaks (ppm)	assignment	peaks (ppm)	assignment
1.7	CH_2s between O-CH_2 and N-CH_2	3.1	three N-methyl
4.2	O-methylene	3.5	N-methylene
5.5 - 6.5	vinyl protons	7.0 - 7.2	aromatic protons from diaminobenzene ring
9.0 - 9.5	aromatic protons from 2,5-dinitrobenzoic acid ring		
10.8	OH		

Comparing the two groups of peaks in table 2.5, it is noted that the peaks change dramatically with temperature are all highly related to the diaminobenzene group.

The N-methyls and the N-methylene peaks from 3.1 to 3.5ppm are broadened when temperature is higher than 20°C, and became sharp when temperature is lower than 20°C.

The aromatic protons (7.0 - 7.2ppm) from diaminobenzene ring showed the similar behaviour to that of N-methyl and N-methylene.

The N-methyl, N-methylene and aromatic protons are not directly connected with nitrogen, therefore the line broadening of these peaks are not due to quadrupole effect.

When the NMR sample was prepared under argon gas, and spectrum was recorded under argon protection, there was no line broadening phenomenon. This indicated that oxygen is one reason for the line broadening as proved by some other researcher that oxygen can oxidize the neutral diaminobenzene group to its radical cation form.[116]

In a NMR sample without argon protection, the radical cation form of the monomer is present in the NMR sample due to oxidation by air. Therefore the electron exchanging between the neutral form and the radical cation form is inevitable. From equation 2.1, it can be seen that the peak width is proportional to the electron exchanging rate. The electron exchanging rate increase with the temperature, therefore causing in the broadening of peaks at high temperature.

The peak at 1.7ppm did not change much from 50 to - 50°C, except for that at -50°C two peaks were observed, suggesting that the broad peak at this chemical shift is caused from the overlapping of two methylene peaks (CH_2-C-N and CH_2-C-O).

The O-methylene and vinyl peaks remained unchanged when temperature is higher or lower than 20°C. Because the O-methylene and vinyl groups are far away from the diaminobenzene group, they are not affected by the electron exchanging of the diaminobenzene group and its radical cation form.

The aromatic peaks from 2,5-dinitrobenzoic acid remained sharp, indicating no electron exchanging between 2,5-dinitrobenzoic acid and the monomer, further more it suggested that 2,5-dinitrobenzoic acid does not form charge-transfer complex with the monomer (104).

The broad OH peaks is due to proton exchanging as expected. The chemical shift varied at different temperatures, because the OH proton is very sensitive to experimental conditions.

The broad peaks in the ^{1}H-NMR spectra for toluenesulphonic acid salt (99) (102) are only the N-methyl, N-methylene and aromatic protons from the diaminobenzene ring too. Therefore the line broadening in those spectra are due to the electron exchanging between the diaminobenzene group and its radical cation form.

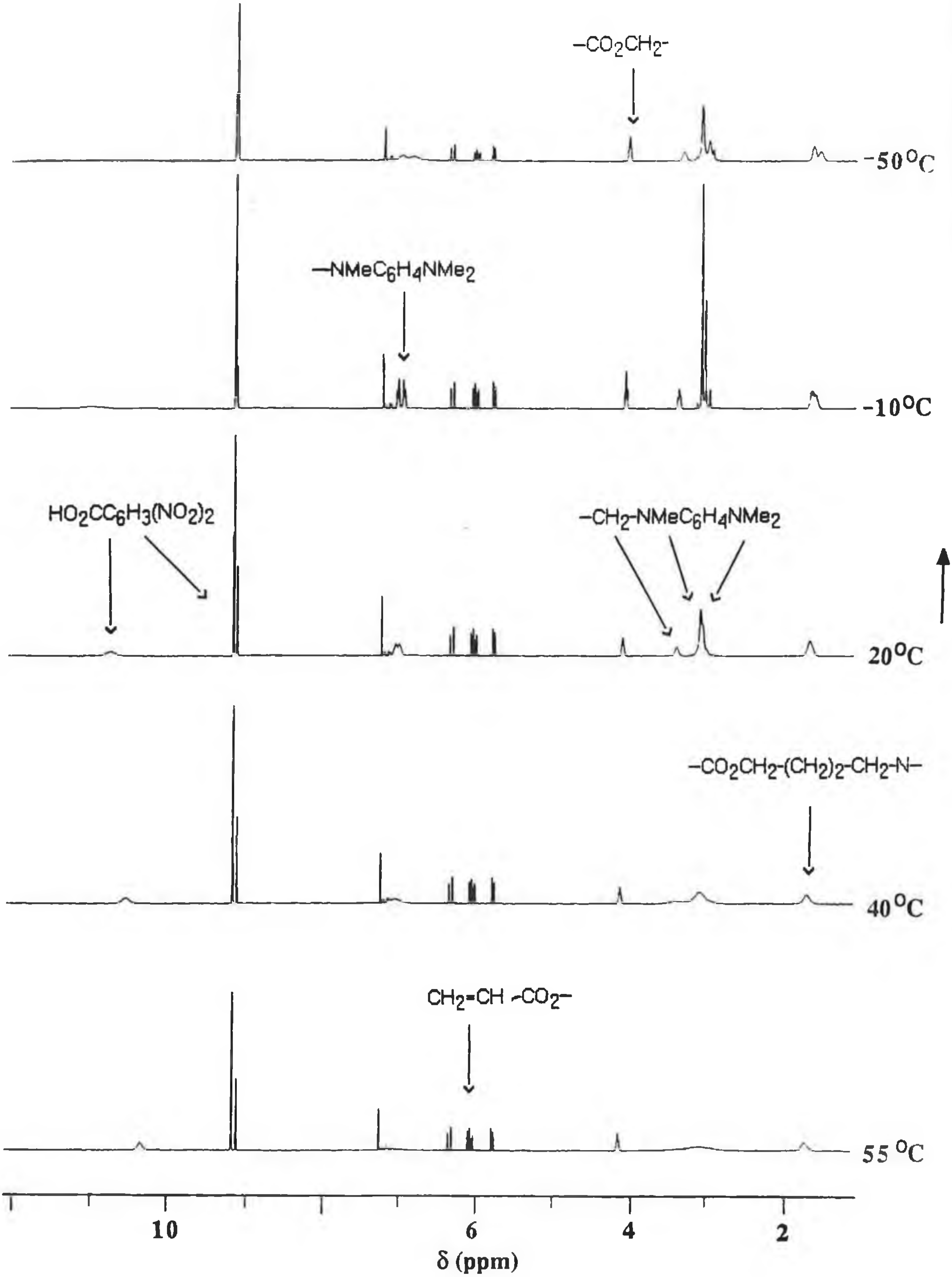
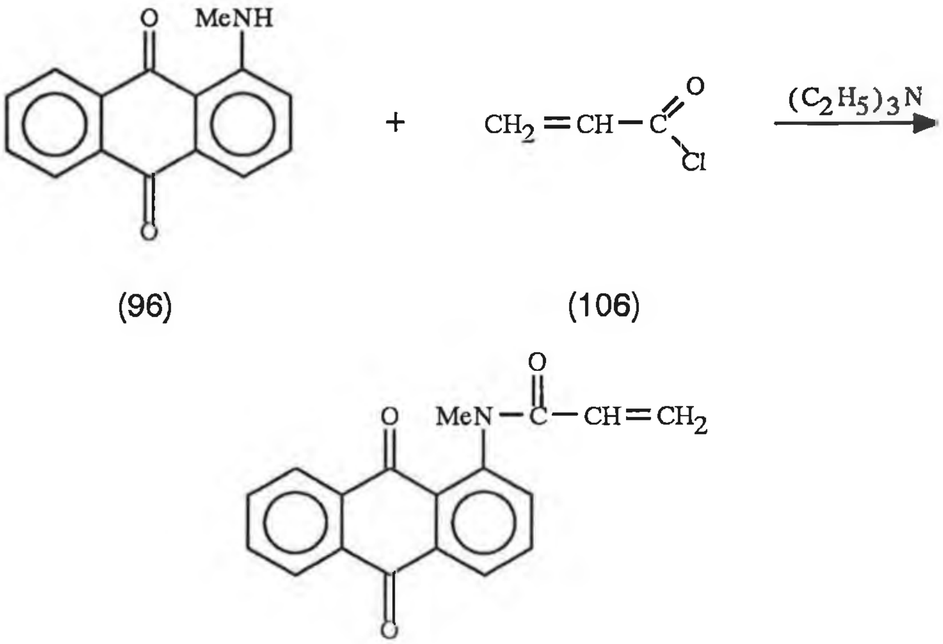


Figure 2.4 ^{1}H-NMR spectra at various temperatures for (105)

2.4.10 Synthesis and characterisation of N-aryloyl-N-methyl-1-aminoanthraquinone



(96) (106)

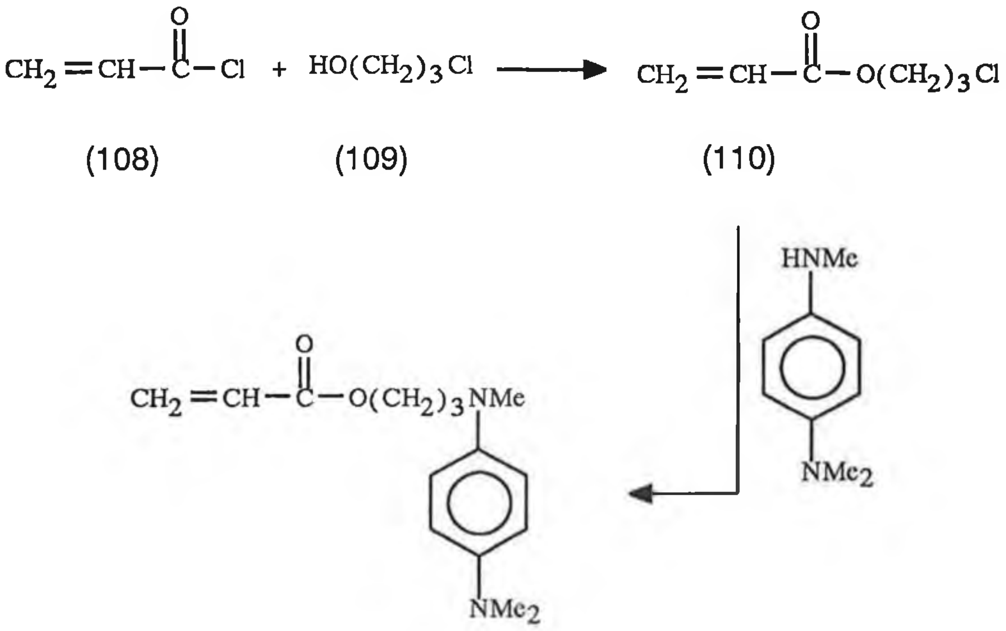
(107)

Reaction of acryloyl chloride (106) in chloroform with N-methyl-1-aminoanthraquinone (96) in the presence of triethylamine gave the required product (107). In the ^{1}H-NMR spectrum the three protons of the vinyl group showed the expected pattern in the range from 5.3 to 6.7ppm. The singlet at 3.37ppm was due to the methyl group. The peaks from 7.5 to 8.5ppm corresponded to the seven aromatic protons. The ^{13}C-NMR spectrum was also consistent with the product having structure of the product (107) (see experimental section).

2.4.11 Some other attempts to synthesize diaminobenzene type monomers

In this section some other reactions which were attempted, but did not succeed, will be discussed.

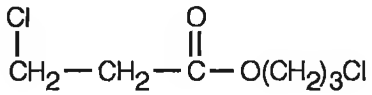
Before the tosylate group was used as a leaving group in the nucleophilic substitution reactions with p-dimethylamino-N-methylaniline (77), the use of chloride as leaving group was studied. The following reaction sequence seemed potentially useful as a route to the required monomers.



(108) (109) (110)

(111)

Reaction of acryloyl chloride (108) with 3-chloropropanol (109) gave a mixture of two products which were separated by distillation. These were identified as 3-chloropropyl acrylate (110) (yield 28%) and 3-chloropropyl-β-chloropropionate (112) (yield 21%).



$ClCH_2-CH_2-C(=O)-O(CH_2)_3Cl$

(112)

In the ^{1}H-NMR of compound (110), the 2-methylene group appeared at 2.12ppm as a two proton quintet (J=6.0 Hz), the Cl-methylene at 3.62ppm as a two proton triplet (J=6.0 Hz), the O-methylene group at 4.30ppm as a two proton triplet (J=6.0 Hz), and the vinyl group at 5.5 - 6.5ppm as a three proton multiplet.

In the ^{1}H-NMR spectrum of compound (112), there were methylene absorption at 2.12ppm (quintet, J=6.0 Hz, $ClCH_2$), 3-methylene 2.81ppm (triplet, J=6.6Hz), 3.62ppm (triplet, J=6.0 Hz, $ClCH_2$), 3.78ppm (triplet, J = 6.6 Hz, CH_2CO), and at 4.30ppm (triplet, J=6.0 Hz, OCH_2).

The reaction of 3-chloropropyl acrylate with p-dimethylamino-N-methylaniline did not give the required compound at relatively low temperature (60^{o}C). At higher temperature (100 ^{o}C) however a polymerization reaction occurred to yield an intractable material. This scheme was not investigated further since subsequent investigation identified the tosylate sequence as being superior.

2.4.12 Investigations of the synthesis of some hydroquinone type monomers

Hydroquinone is a well known redox function,[55] polyvinyl hydroquinone have been made by many authors in different ways.[7, 55]

Our purpose is to make some hydroquinone monomers analogous to the p-diaminobenzene type ones which have been synthesised in this work.

Literature investigation gave no indication of good synthesis of 2-hydroxymethylene hydroquinone which could be used as a good starting materials.

However literature[118] showed that the reaction of (114) with acetic anhydride give methyl acetate-2-hydroquinone. It seemed possible that the route could be modified to yield (115). Using the reaction scheme described below it was anticipated that the hydroquinone moiety could be simply introduced into a polymerible monomer. Although, the goal to synthesize the monomer was not reached, some intermediate compounds were well characterized.

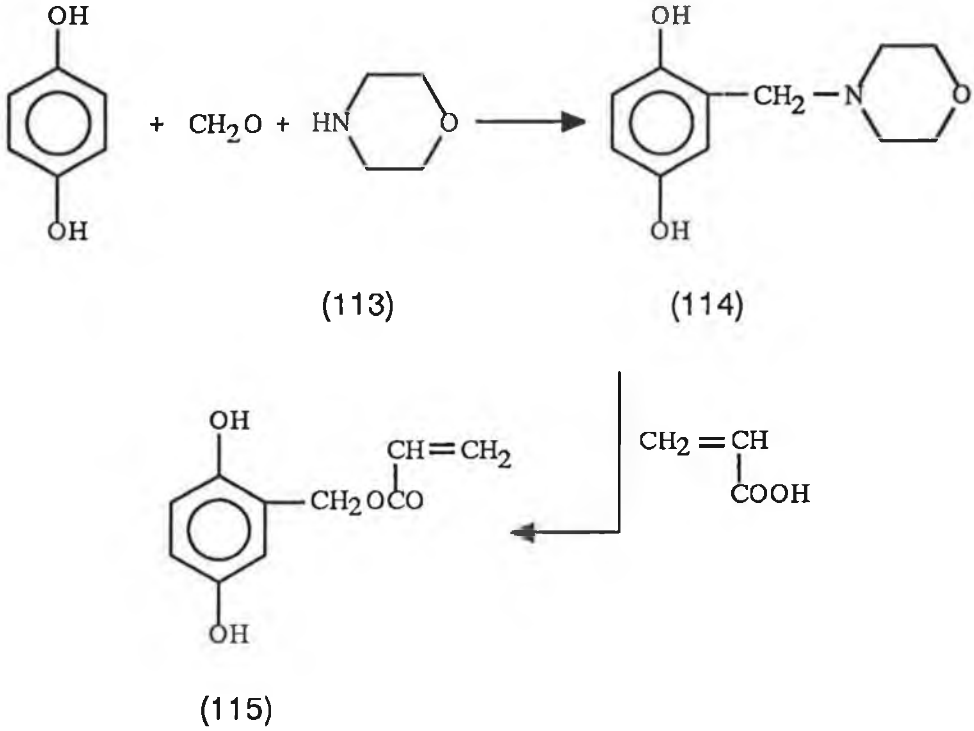
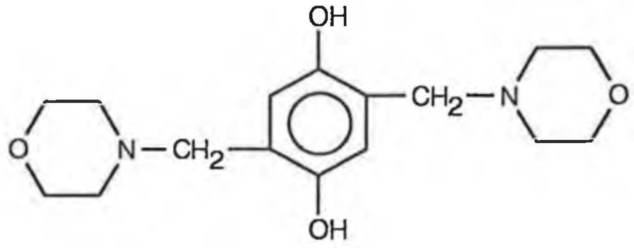


Figure 2.5 The reaction scheme intended to synthesize hydroquinone type monomers

In this scheme, the first step was a Mannich-type condensation reaction. The reactivity of the hydroquinone made it difficult to ensure clean formation of the required product (114)[118]. At relatively low temperature, (< 25 ^{o}C), the main product of the reaction of equimolar amounts of paraformaldehyde and morpholine with hydroquinone was the required 2-morpholinomethylhydroquinone (114), However a byproduct 2,5- bis(morpholinomethyl)hydroquinone (116) was also produced.[118] It was quite difficult to separate the two compounds by repeated recrystallization alone. However the solubility of 2,5-bis(morpholinomethyl)hydroquinone (116) in chloroform was much greater than that of 2-morpholinomethylhydroquinone (114). Recrystallization of the crude product from ethyl acetate, following by chloroform washing gave analytically pure 2-morpholinomethylhydroquinone (114) (38% yield). From the chloroform mother liquid 2,5-bis(morpholinomethyl)hydroquinone (116) could be isolated in 11% yield, after recrystalization from ethyl acetate. However 2,5-bis(morpholinomethyl)hydroquinone (116) could be more conveniently synthesized by treatment of hydroquinone with two molar equivilents each of amine and formaldehyde at 50°C.



(116)

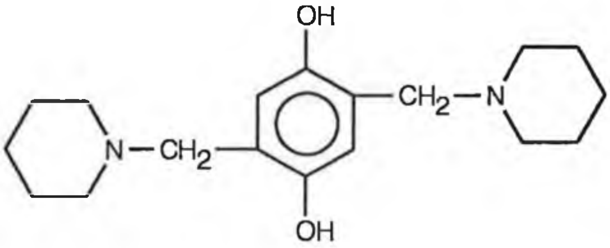
NMR spectroscopy confirmed the structures of compounds (114) and (116). In the ^{1}H-NMR spectrum of 2-morpholinomethylhydroquinone (114), the four proton singlet at 2.53ppm was assigned to the N-methylene protons in the morpholine ring, the two proton singlet at 3.63ppm to the methylene group linking the nitrogen to the aromatic ring, the four proton singlet at 3.74ppm to the O-methylene protons in the morpholine ring, the three proton multiplet from 6.4 - 6.7ppm to the aromatic protons in the hydroquinone ring, and the broad two proton signal at 7.50ppm to the OH groups..

In the ^{13}C-NMR spectrum of 2-morpholinomethylhydroquinone (114), the N-methylene groups in the morpholine ring appeared at 52.81ppm, the N-methylene linking the morpholine group to hydroquinone ring at 61.66ppm, and the O-methylene groups at 66.77ppm. In this compound the aromatic ring is not symmetric, therefore the chemical shifts of the six aromatic carbons were all different, appearing at 115.50 , 115.75, 116.61, 121.45, 148.76, and 150.62ppm.

The aromatic ring of tetrasubstituted hydroquinone (116) is symmetric, and its NMR spectra were simpler than those of (114). In the ^{1}H-NMR spectrum of (116), the eight proton singlet at 2.55ppm was assigned to the N-methylenes of the morpholine rings, the four proton singlet at 3.65ppm to the N-methylenes linking the morpholines to the aromatic ring, the eight proton singlet to the O-methylenes, the two proton singlet at 6.50ppm to the aromatic protons, and the broad two protonsignal at 10.05ppm to OH groups.

In the ^{13}C-NMR spectrum of 2,5-bis(morpholinomethyl)hydroquinone (116) the N-methylenes of the morpholine ring appeared at 52.91ppm, the N-methylenes group between the morpholines and the aromatic ring appeared at 61.57ppm, the O-methylenes at 66.78ppm, and the three different aromatic carbons at 116.07, 120.84, and 149.90ppm.

This Mannich condensation reaction also occurred with piperidine. However only 2,5-bis(piperidinomethyl)hydroquinone (117) was obtained, even from room temperature reaction involving equimolar proportions of piperidine, formaldehyde and hydroquinone. The reaction of two equivilents each of amine and formaldehyde with hydroquinone provided a convenient synthesis of (117). The ^{1}H and ^{13}C-NMR spectra of this compound were consistent with the tetrasubstituted structure (117).



(117)

Reaction of 2-morpholinomethylhydroquinone (114) with acrylic acid in toluene did not give the required compound (115), only gave a salt. Addition of aqueous sodium hydroxide into the salt can liberate the compound (114). When temperature was over 50^{o}C, acrylic acid was polymerized under nitrogen, without nitrogen the substituted hydroquinone was oxidised. In order to simplify the situation, acetic acid was used instead to react with

2-morpholinomethylhydroquinone to avoid the polymerisation problem. The reaction of 2-morpholinomethylhydroquinone with acetic acid at 100°C with mineral acid as catalysis did not give the substituted compound (only gave a salt) suggested that the morpholino group in compound (114) is not easy to be substituted by a nucleophile. Addition of aqueous sodium hydroxide solution to the salt, compound (114) was isolated.

Acetyl chloride and methyl iodide were used to form salts with (114) first then react with acetic acid. It was expected that the salts formed should be easier to be attacked by acetic acid, and the morpholino group should leave more easily. However, the experiments showed the required compound was not produced. indicating again the morpholino group is not easy to be substituted by some other nucleophile.

2.5 Experimental section

2.5.1 General experiments

NMR spectra were recorded on either a Jeol EX270 or a Bruker AC-400 instrument operating at 270MHz/400MHz for ^{1}H-NMR and 67.8MHz/100MHz for ^{13}C-NMR, respectively in $CDCl_3$, .

Infrared spectra were recorded on a Perkin-Elmer 983G infrared spectrophotometer.

Ultra-violet absorption spectra were recorded on a Hewlett Packard 8452A diode array UV-vis spectrophotometer.

Thin layer chromatography (TLC) was carried out on silica gel TLC plates containing a fluorescent indicator (Riedel-de-Haen, DC-Cards Si F, layer thickness 0.2mm).

Elemental analyses were carried out by the Microanalytical Laboratory, University College Dublin.

2.5.2 Preparation of N-succinimidomethyl-p-dimethylaminoaniline (85)

Succinimide (11.89g, 0.12mol, 20% excess) dissolved in hot ethanol (100cm^3) and p-dimethylaminoaniline (13.70g, 0.10mol) in hot ethanol (50cm3) were mixed in a flask. The solution was allowed to cool to approx. 45^{o}C. Formaldehyde (9.6cm^3, 35-37% aqueous solution, 0.125mol, 25% excess, RDH) was added slowly. a precipitate formed immediately. After addition of all the formaldehyde, the mixture was refluxed for 1.5 hours, during which the precipitate dissolved. The mixture was cooled to 45^{o}C and the precipitate filtered off giving compound (85)(12.39g, 47%). Three recrystallization from ethanol gave analytical pure sample. Melting point was 139.5 - 140.0^{o}C.

IR (KBr pellet): 3367 (N-H), 3073, 3024, 2990, 2955, 2889, 2799, 1838, 1763, 1688 (C=O), 1531, 1484, 1445, 1414, 1352, 1297, 1265, 1250, 1211, 1201, 1140, 1126, 1114, 1073, 1059, 1003, 942, 814, 737, 711, 667, 647, and 633cm^{-1}.

^{1}H-NMR: δ 2.60 (s, 4H), 2.79 (s, 6H), 4.50 (sb,1H) (disappeared on addition of D_2O), 4.92 (d, J=0.8Hz, 2H), 6.65-6.75 (m, 4H)ppm

^{13}C-NMR: 28.03, 41.72, 49.72, 115.17, 115.31, 136.01, 145.06, and 177.51ppm

Found: C 63.01; H, 6.95; N, 17.00%. $C_{13}H_{17}N_3O_2$ requires C, 63.07, H 6.88, N 16.98%.

2.5.3 Preparation of N-methyl-p-dimethylaminoaniline (77)

N-succinimidomethyl-p-dimethylaminoaniline (85) (12.37g, 0.05mol) was dissolved in DMSO (100cm^3) by heating, sodium borohydride (2.08g, 0.055mol, 10% excess) was added in portions. Sodium dithionite (5mg) was added to suppress oxidation. After 10 minutes at 100^{o}C, ice (150g) was added to quench the reaction. The solution was extracted three times using ether (100 cm^3 each time). The ether extract was backwashed with saturated sodium chloride solution (100 cm^3). After drying over magnesium sulphate, solvent was removed to give N-methyl-p-dimethylaminoaniline (77) (5.30g 71%). Further purification of (77) was carried out by distillation under reduced pressure, b.p. 118.0-119.0^{o}C/5mm in a nitrogen atmosphere (lit.[105] 265^{o}C).

IR (coated on NaCl plate): 3388 (N-H), 2926, 2870, 2791, 1826, 1615, 1514, 1469, 1445, 1396, 1301, 1260, 1211, 1152, 1110, 1054, 1002, 944, 914, and 719cm^{-1}.

^{1}H-NMR: δ 2.64 (s, 3H), 2.74 (s, 6H), 3.33 (s, 1H), 6.49 (d, J=9Hz, 2H), 6.69 (d, J=9 Hz, 2H). Addition of D_2O caused the disappearance of singlet at 3.33ppm.

^{13}C-NMR: 31.17, 41.86, 113.36, 115.57, 141.83, and 143.47ppm.

Found: C, 71.83; H, 9.42; N 18.47%. $C_9H_{14}N_2$ requires C, 71.96; H, 9.39; N,18.65%.

2.5.4 Preparation of N,N'-bis(succinimidomethyl)-p-diaminobenzene (86)

Succinimide (23.78g, 0.24mol, 20% excess) and p-diaminobenzene (10.81g, 0.10mol) dissolved in hot ethanol (100cm^3), were mixed together. The solution was allowed to cool to 50^{o}C. Without heating but with stirring, formaldehyde solution (19.1 cm^3, 35- 37% aq., 0.25mol, 25% excess) was added slowly. A precipitate formed immediately. On completion of the addition of formaldehyde, the solution was refluxed for ten minutes and then cooled. The precipitate was collected to give N,N'- bis(succinimidomethyl)-p-diaminobenzene (86) (32.56g, 99%). Compound (86) is not soluble in ethanol, water, chloroform, acetone, ethyl acetate or THF, only soluble in hot DMF or DMSO.

2.5.5 Acetylation of N,N'-bis(succinimidomethyl)-p-diaminobenzene(86)

N,N'-Bis(succinimidomethyl)-p-diaminobenzene (86) (10.0g, 0.03mol) was added to acetic anhydride (20 cm^3) at 100°C in portions. After it had all dissolved, the solution was kept at 100°C for ten more minutes. Crystals formed after 20 hours standing at room temperature and the product (7.87g, 63.0%) was collected by suction filtration. Analytical pure (88) (m.p. 241-243°C) was obtained by recrystallization from acetonitrile.

IR (KBr pellet): 3469, 3318, 3065, 3040, 3026, 2985, 2938, 1783(C=O), 1736(C=O), 1512, 1360, 1303, 1184, 1102, 1082, 1035, 1021, 996, 966, 886, 863, 855, 815, 696, 666, and 632 cm^{-1}.

^1H-NMR: δ 1.83 (s, 6H), 2.51 (s, 8H), 5.35 (s, 4H), and 7.17 (s, 4H)ppm.

^{13}C-NMR (CD_3CN): 21.65, 27.41, 48.73, 129.84, 139.84, 169.07, 176.48ppm.

Found: C, 58.04; H, 5.32; N 13.52% . $C_{20}H_{22}N_4O_6$ requires C, 57.97; H, 5.35; N, 13.52%.

2.5.6 Preparation of N,N'-dimethyl-p-diaminobenzene (87)

N,N'-Bis(succinimidomethyl)-p-diaminobenzene (86) (16.52g, 0.05mol) was dissolved in DMSO (100cm^3) at 140°C. It was allowed to cool to 80°C, then sodium borohydride (4.15g, 0.11mol, 10% excess) was added in portions. Sodium dithionite (5mg) was added to suppress oxidation. After 10 minutes at

100°C, ice (200g) was added to quench the reaction. The solution was extracted with diethyl ether (three times, 100cm^3 each time) which was then backwashed with saturated aqueous sodium chloride solution (100cm^3). Dried over magnesium sulphate, the diethyl ether was removed to give crude N,N'-dimethyl-p-diaminobenzene (87) (4.76g, 70%). This was passed through a silica gel column. Elution with a mixed solvent (light petroleum (40-60°C) : diethyl ether = 1:2) followed by removal of the solvent gave solid N,N'-dimethyl-p-diaminobenzene (87) which was recrystallized from light petroleum(40-60°C) to give pure (87) (3.88g, 57%), m.p. 52-53°C (lit.[106], 53°C).

IR (cast from chloroform on NaCl plate): 3275 (N-H), 3028, 2975, 2885, 2800, 1518, 1466, 1449,1399, 1300, 1251, 1152, 1120, 1097, 921, and 812cm^{-1}.

^{1}H-NMR: δ 2.74 (s, 6H), 3.28 (s, 2H), 6.53 (s, 4H). Addition of D_2O caused the disappearance of the singlet at 3.28ppm.

^{13}C-NMR 31.17, 113.36, 141.83ppm.

Found C, 70.88; H, 9.10; N, 20.70%. $C_8H_{12}N_2$ requires C, 70.55; H, 8.88; N, 20.57% .

2.5.7 Preparation of N, N'-bis(succinimidomethyl)-o-diaminobenzene (90)

Succinimide (23.78g, 0.24mol, 20% excess) and o-diaminobenzene(10.81g, 0.10mol) each dissolved separately in hot ethanol (70cm^3) were mixed together. The mixture was allowed to cool to 50°C. Formaldehyde (19.1cm^3, 35-37% aqueous solution, 0.25mol, 25% excess) was added slowly. After five minutes, a grey precipitate formed. The mixture was refluxed for 1 hour, and then the precipitate was filtered when hot. Recrystallization from chloroform gave white crystals of (90) (17.00 g, 51.47%), m.p. 174.0-175.0°C.

IR (KBr pellet): 3434 (N-H), 2962, 1768, 1687 (C=O), 1602, 1547, 1489, 1458, 1413, 1350, 1317, 1269, 1251, 1205, 1147, 1125, 1082, 1064, 1003, 949, 927, 823, 760, 746, 669, and 642 cm^{-1}

^{1}H-NMR δ 2.62 (s, 8H), 4.62 (t, J=5.4Hz 2H), 4.95 (d, J=5.4Hz, 4H) and 6.8 (s, 4H)ppm. Addition of D_2O caused the disappearance of the peak at 4.62ppm.

^{13}C-NMR ($CDCl_3$): 28.13, 49.20, 116.27, 121.58, 134.36, and 177.64ppm. The off-resonance decoupled spectrum showed the peaks at 28.13ppm and 49.20ppm as triplets, the peaks at 116.27 and 121.58ppm as doublets and the peaks at 134.36 and 177.64ppm remained as singlets.

Found C, 58.14; H, 5.48; N, 16.80%. $C_{16}H_{18}N_4O_4$ requires C, 58.17; H, 5.49; N, 16.96%.

2.5.8 Preparation of N,N'-dimethyl-o-diaminobenzene (91)

N,N'-Bis(succinimidomethyl)-o-diaminobenzene (90) (16.52g, 0.05mol) was dissolved in DMSO (100cm^3) at room temperature, then sodium borohydride (4.15g, 0.11mol, 10% excess) was added in portions. The solution was heated and the sodium borohydride dissolved slowly. Sodium dithionite (5mg) was added to suppress oxidation. After 15 minutes at 100^{o}C, 200g of ice was added to quench the reaction. Diethyl ether (3X100cm^3) was used to extract the solution. The extract was then backwashed with saturated aqueous sodium chloride solution (100cm^3). After drying over magnesium sulphate, the solvent was removed to give a liquid. Distillation under reduce pressure in a nitrogen atmosphere gave N,N'-dimethyl-o-diaminobenzene (91) (4.70g, 69%), b.p. 104^{o}C/4mm (lit.[106]108.5-109.0^{o}C/5mm)

IR (liquid film on NaCl plate): 3347 (N-H), 3053, 2982, 2942, 2883, 2808, 2612, 1601, 1514, 1479, 1442, 1340, 1307, 1266, 1226, 1166, 1126, 1094, 1042, 901, 927, 738, and 630cm^{-1}.

^{1}H-NMR: δ 2.74 (s, 6H), 3.21 (s, 2H), 6.60 (m, 2H), and 6.80 (m, 2H)ppm. Addition of D_2O caused the disappearance of singlet at 3.21ppm.

^{13}C-NMR: 30.79 110.13, 118.80, and 138.09ppm

Found C, 70.29; H, 8.97; N, 20.57%. $C_8H_{12}N_2$ requires C, 70.55%; H, 8.88; N, 20.57%.

2.5.9 Attempted synthesis of N, N'-bis(succinimidomethyl)-m-diaminobenzene

Succinimide (23.78g, 0.24mol, 20% excess) and m-diaminobenzene(10.81g, 0.10mol) each dissolved separately in hot ethanol (80cm^3) were mixed together. The mixture was allowed to cool to 50°C. Formaldehyde (19.1cm^3, 35-37% aqueous solution, 0.25mol, 25% excess) was added slowly. A light yellow precipitate formed immediately. After ten more minutes heating the precipitate was filtered when hot. This yellow precipitate was washed three times and dried under vaccuum to give 8.5 g product. The solubility of this yellow in all the common solvents were very poor and recrystallization of this sample was impossible. It can only dissolve in hot DMSO (100°C). The reaction of this yellow substance with sodium borohydride in DMSO (100°C) did not give N,N'-dimethyl-m-benzeze. Only the starting material was recoved from the reaction solution.

IR (KBr pellet): 3341, 2846, 1613, 1512, 1300, 1207, 1129, 990, 833, and 690cm^{-1}

m-Diaminobenzene (10.81g, 0.10mol) was dissolved in hot ethanol ($100cm^3$), and the solution was allowed to cool to 50°C. Formaldehyde ($19.1cm^3$, 35-37% aqueous solution, 0.25mol) was added slowly. A light yellow precipitate formed immediately. After ten more minutes heating the precipitate was filtered when hot. This yellow precipitate was washed three times and dried under vaccuum to give 7.6 g product. The solubility of this yellow substance in all the common solvents were very poor and recrystallization of this sample was impossible.

IR (KBr pellet): 3340, 2845, 1617, 1511, 1300, 1202, 1129, 988, 831, and $690cm^{-1}$

2.5.10 Preparation of N-succinimidomethyl-1-aminoanthraquinone (95)

Due to the poor solubility of 1-aminoanthraquinone (94) in ethanol, DMF was used as solvent instead in this reaction. 1-Aminoanthraquinone (22.3g, 0.1mol) was dissolved in DMF ($300cm^3$) at 100°C. Succinimide (11.89g 0.12mol) dissolved in DMF ($50cm^3$) was then added. At 100 °C, formaldehyde ($9.6cm^3$, 35-37% aqueous solution, 0.125mol) was added slowly with stirring. After about 5 minutes a thick orange precipitate formed. After 10 more minutes heating, the solution was cooled down, and the precipitate was filtered off to give (95) (28.16g, 88%) which was washed four times with ethanol. The solubility of (95) in all the common solvents (including DMSO) were very poor and recrystallization of this sample was impossible. The compound was used directly in the reduction step of the synthesis without further purification. m.p. 265-266°C.

IR (KBr pellet): 3251, 3073, 1710 (C=O), 1670 (C=O), 1631(C=O), 1590, 1500, 1409, 1374, 1357, 1271, 1179, 1121, 1075, 1043, 983, 883, 859, 826, 801, 770, 733, 705, and $658cm^{-1}$

5.11 Preparation of N-methyl-1-aminoanthraquinone (96)

N-Succinimidomethyl-1-aminoanthraquinone (95) (8g, 0.025mol) and DMSO (150cm^3) were added to a flask. The orange solid did not completely dissolve at 100^{o}C. When sodium borohydride (2.08g, 0.0275mol, 10% excess) was added slowly to the suspension at 100^{o}C, the orange solid disappeared gradually. The solution was stirred at 100^{o}C for 10 more minutes. Ice (200g) was added to quench the solution. Chloroform (3X100cm^3) was used to extract the solution, and the extract was backwashed with saturated sodium chloride solution (100cm^3). Dried over anhydrous magnesium sulphate, the solvent was removed to give a red solid (5g, 84%). Three times recrystallizations from light petroleum (60-80^{o}C) gave an analytical pure sample of N-methyl-1-aminoanthraquinone (96), m.p. 167-168^{o}C (lit.[110] 170^{o}C).

IR (KBr pellet): 3303 (N-H), 3067, 2907, 2836, 1672 (C=O), 1630 (C=O), 1593, 1566, 1505, 1462, 1423, 1396, 1360, 1312, 1271, 1234, 1180, 1159, 1088, 1071, 987, 859, 828, 808, 777, 733, 709, and 663cm^{-1}.

^{1}H-NMR: δ 3.05 (s, 3H), 7.05 (d, J = 7.98 Hz, 1H), 7.57 (t, J = 7.92 Hz, 1H) , 7.61 (d, J = 7.38 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.77 (t, J = 7.4 Hz, 1H), 8.24 (d, J = 7.60 Hz, 1H), 8.27 (d, J = 7.60 Hz, 1H), and 9.65 (bs, 1H)ppm. addition of D_2O caused the disappearance of the broad singlet at 9.65ppm. The COSY spectrum showed coupling of the peaks grouped around 7.05 with those around 7.59ppm, and coupling of the group of peaks around 7.74 with that around 8.25ppm.

^{13}C-NMR: 29.57, 112.98, 115.54, 117.38, 126.63, 126.66, 132.87, 132.97, 133.88, 134.50, 134.93, 135.28, 152.46, 183.78, and 184.90ppm.

Found C, 75.63; H, 4.57; N, 5.71% . $C_{15}H_{11}O_2N$ requires: C, 75.94; H, 4.67; N 5.9%.

2.5.12 Tosylation of 2-hydroxyethyl methacrylate (72)

2-Hydroxyethyl methacrylate (72) (39.00g, 0.3mol) and pyridine (96cm^3, dried over potassium hydroxide) were placed in a flask which was surrounded with ice. p-Toluenesulphonyl chloride (62.88g, 0.33mol) was added in portions at such a rate that the temperature did not rise above 20^{o}C. The mixture was stirred for an additional three hours with ice cooling. During this time a white precipitate formed (possiblly pyridine hydrochloride).

Water (50 cm^3) was added to the reaction mixture and the solid dissolved. The solution was then extracted with diethyl ether three times (50 cm^3 each time). The combined extracts were thoroughly washed with water , dilute hydrochloric acid and finally water until the pyridine was removed. It was then dried over anhydrous magnesium sulphate. Removal of the solvent gave liquid tosylate(97) (73.00g, 86%). TLC (diethyl ether) showed one spot, different from the starting materials.

IR (liquid film) 2940, 1710(C=O), 1620, 1585, 1440, 1390, 1350, 1310, 1280, 1160, 1100, 1080, 1000, 940, 910, 800, 755, and 650cm^{-1}

^{1}H-NMR ($CDCl_3$, 60MHz): δ 1.86 (s, 3H, methyl attached to the double bond), 2.42 (s, 3H, methyl attached to the aromatic ring), 4.26 (s, 4H, 2CH_2), 5.54 (s, 1H, vinyl), 6.02 (s, 1H, vinyl), 7.32 (d, 2H, J=8.4Hz, aromatic), and 7.80 (d, 2H, J=8.4 Hz aromatic)ppm.

This liquid (97) was used directly for the next stage of the synthesis without further purification.

2.5.13 Synthesis of 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate as its p-toluenesulphonic acid salt (99)

2-(p-Toluenesulphonyloxy)ethyl methacrylate (97) (17.04g, 0.06mol, 50% excess), dry toluene (70cm^3) and anhydrous sodium carbonate (8.00g

0.08mol) were placed into a flask in which the solution was blanketed with nitrogen. Then fresh N-methyl-p-dimethylaminoaniline (77) (6.00g, 0.04mol) was added. The solution was stirred at 50-60°C until TLC (diethylether : light petroleum(b.p. 40-60 °C) =1:2) showed that reaction was nearly completed (43 hours). The reaction mixture was cooled to room temperature. Water (75cm^3) was added and the mixture was then extracted with three 50cm^3 portions of diethyl ether. The ether layer was backwashed once with 50 cm^3 water. p-Toluene sulphonic acid monohydrate (15.2g, 0.08mol) was added to the ether extract with thorough shaking. The organic layer became clear, and a lower red liquid phase separated. Water (20cm^3) was added and the mixture shaken thoroughly. The aqueous layer was separated from the organic layer and washed three times with diethyl ether (40cm^3). This aqueous layer which contained the product was then extracted with chloroform many times. The process of the extraction was monitored by TLC using small samples which had been basified with aqueous sodium hydroxide. The chloroform extract was backwashed once with water (10cm^3), and the chloroform was removed. On standing overnight, a solid was obtained. Four recrystallizations from toluene gave shiny blue crystal of (99) as platelets, melting point 78.0 - 79.5°C (5.86g, 34%).

UV/Vis (ethanol): λ_{max}, 215 (ε 22,310), 265 (21,000), 310(sh) nm(1050).

Infrared (KBr pellet): 3433(br. OH), 3027, 2962, 2925, 2669, 2521, 1914, 1714 (C=O), 1634, 1612, 1524, 1454, 1380, 1320, 1297, 1275, 1184, 1122, 1075, 1052, 1033, 1010, 951, 907, 818 (aromatic para-disubstitution), 684, 619cm^{-1}.

^{1}H-NMR δ 1.87 (s, 3H), 2.34 (s, 3H), 2.98 (s, broad, 3H), 3.14 (s, broad, 6H), 3.63 (s, broad, 2H), 4.27 (s, 2H), 5.54 (s, 1H), 6.02 (s, 1H), 6.72 (s, broad, 2H), 7.18 (d, 2 H), 7.43 (s, broad, 2H), and 7.82 (d,2H)ppm.

^{13}C-NMR: 18.19, 21.26, 39.09, 46.86, 51.05, 61.35, 112.90, 120.89, 125.93, 126.07 128.81, 132.28, 135.78, 140.03, 142.30, 149.00, and 167.15ppm.

Found: C, 60.64; H, 7.28; N, 6.16%. $C_{22}H_{30}O_5N_2S$ requires: C, 60.81; H, 6.96; N, 6.45%

2.5.14 Tosylation of 2-hydroxyethyl acrylate

2-Hydroxyethyl acrylate (73) (34.8g, 0.3mol, Aldrich) and pyridine (97cm^3, dried over potassium hydroxide) were placed into a flask which was surrounded with ice. p-Toluene sulphonyl chloride (62.89g, 0.33mol) was added in portions at such a rate that the temperature did not rise above 20 ^{o}C. The mixture was stirred for an additional three hours with ice cooling. Water (50cm3) was added to the reaction mixture and the solution was removed into a separating funnel. Two phases were separated. The bottom layer was collected and thoroughly washed with water until pyridine was removed. Then it was dissolved in diethyl ether and dried over anhydrous magnesium sulphate. Removal of the solvent gave liquid (100) (60.4g , 74%), which TLC showed one spot on TLC, different from the starting materials.

IR (liquid film): 2964, 1723 (C=O), 1635, 1639, 1599, 1448, 1410, 1359, 1297, 1273, 1180, 1121, 1098, 1065, 1021, 942, 889, 813, 791, 737, 689, 664cm^{-1}.

^{1}H-NMR (CDCl$_3$, 60 MHz): 2.40(s, 3H, Me), 4.26 (s, 4H, 2XCH$_2$), 5.6-6.5 (m, 3H, vinylic H), 7.1-7.9 (2d, 4H, aromatic).

This liquid was used directly for the next stage of the synthesis without further purification.

2.5.15 Preparation of 2-(p-dimethylamino-N-methylanilino)ethyl acrylate as its p-toluenesulphonic acid salt (102)

2-(p-Toluenesulphonyloxy)ethyl acrylate (100) (47.88g, 0.176mol, 10% excess) was dissolved in 200 cm^3 toluene, and anhydrous sodium carbonate (32.00g, 0.32mol) was added. The flusk was flashed with dry nitrogen and a positive nitrogen pressure was maintained throughout the subsequent reaction. The temperature was raised to 60^{o}C, and freshly prepared N-methyl-p-dimethylaminoaniline (77) (24g, 0.16mol) was added. The reaction solution was stirred until TLC (diethylether : light petroleum (b.p. 40-60 ^{o}C) =1:2) showed that reaction was nearly completed (42 hours). The reaction mixture was cooled to room temperature. Water (100cm^3) was added and the mixture was then extracted with three 100 cm^3 portions of diethyl ether. The ether layer was backwashed once with 100 cm^3 water. p-Toluene sulphonic acid monohydrate (60.80g, 0.32mol) was added to the ether extract with thorough shaking. The organic layer became clear, and a lower red liquid phase separated. Water (50cm^3) was added and the mixture shaken thoroughly. The aqueous layer was separated from the organic layer and washed three times with diethyl ether (40cm^3). This aqueous layer which contained the product was then extracted with chloroform many times. The process of extraction was monitored by TLC using small samples which had been basified with aqueous sodium hydroxide. The chloroform extract was backwashed once with water (30cm^3), and the chloroform was removed. On standing overnight, a solid was obtained. Four recrystallizations from toluene gave shiny blue crystal of (102) as platelets (20.19g, 30%), m.p. 65-66^{o}C.

UV/Vis (ethanol): λ_{max} 215 (ε 20600), 265 (20100) , and 310(sh) nm, (820).

IR (KBr pellet): 3431 (br. OH), 3047, 2959, 2515, 1942, 1722 (C=O), 1634, 1616, 1599, 1515, 1493, 1471, 1413, 1349, 1298, 1231, 1118, 1067, 1030, 1007, 928, 904, 866, 830, 813 (aromatic para-disubstitution), 748, 714, and 681cm^{-1}.

^{1}H-NMR: δ 2.34 (s, 3H), 2.97 (s, broad, 3H), 3.15 (s, broad, 6H), 3.63 (s, broad,2H), 4.27 (s, broad, 2H), 5.81 (d, 1H, J=10.52 Hz), 6.06 (dd, 1H, J=17.22, J=10.52), 6.33 (d, 1H, 17.22), 6.18 (s, broad, 2H), 7.18 (d, 2H, J = 7.86 Hz), 7.43 (s, broad, 2H), 7.81 (d, 2H, J = 7.86 Hz)ppm.

^{13}C-NMR 21.26, 39.16, 46.81, 51.10, 61.09, 112.99, 120.82, 125.93, 127.89, 128.82, 131.33, 132.28, 140.05, 142.29, 148.00, 165.89ppm.

Found: C, 59.70; H, 6.76; N, 6.37%. $C_{21}H_{28}O_5N_2S$ requires C, 59.98; H, 6.71; N, 6.66%.

2.5.16 Tosylation of 4-hydroxybutyl acrylate(74)

4-Hydroxybutyl acrylate (74) (36.00g, 0.25mol) and pyridine (81cm^3, dried over potassium hydroxide) were placed in a flask which was surrounded with ice. p-Toluene sulphonyl chloride (52.40g, 0.275mol, 10% excess) was added in portions at such a rate that the temperature did not rise above 20^{o}C. The mixture was stirred for an additional three hours with ice cooling. Water (50cm^3) was added to the reaction mixture and the solution was removed into a separating funnel. Two phases were separated. The bottom phase was collected and thoroughly washed with water until pyridine was removed. Then it was dissolved in diethyl ether and dried over anhydrous magnesium sulphate. Removal of the solvent gave a liquid (103) (49.14g, 69%). TLC (diethyl ether) showed only one spote different from the starting materials.

^{1}H-NMR ($CDCl_3$, 60 MHz): 1.75 (m, 4H, two methylene groups), 2.45 (s, 3H, Me-Ar), 4.1 (m, 4H, CH_2-O), 5.6 - 6.4 (m, 3H, vinyl), 7.1- 7.9 (2d, 4H, aromatic) ppm.

IR(liquid film): 2964, 1723 (C=O), 1635, 1619, 1599, 1495, 1447, 1409, 1359, 1296, 1177, 1121, 1098, 1064, 1020, 1001, 941, 812, 792, 737, 707, 689, 664, and 635cm^{-1}.

This liquid was used directly for the next stage of the synthesis without further purification.

2.5.17 Synthesis of 4-(p-dimethylamino-N-methylanilino)butyl acrylate as its dinitrobenzoic acid salt (105)

2-(p-Toluenesulphonyloxy)butyl acrylate (103) (47.00g, 0.173 mol, 10% excess), anhydrous sodium carbonate (32g, 0.32mol) and dry toluene (140 cm^3) were placed in a flask in which the solution was blanketed with nitrogen. Then freshly prepared p-dimethylamino-N-methylaniline (23.36g, 0.156mol) was added. The solution was stirred at 70°C until TLC showed that reaction was nearly completed (45 hours). The reaction mixture was cooled to room temperature. Water (50cm^3) was added and the mixture was then extracted with two 50cm^3 portions of diethyl ether. The diethyl ether extract was added to a saturated diethyl ether solution of 3,5-dinitrobenzoic acid (66.18g, 0.312mol). After 10 minutes stirring, the mixture was left to stand for 20 hours, and then the solid was collected. Three recrystallisations from toluene-chloroform gave a yellow powder (105) (34g, 31%), m.p. 134.0-135.0 $^\circ$C.

UV/Vis (ethanol): λ_{max} 215 (ε, 103,300), 230 (sh) (61,300), 265 (sh) (45,500), and 320 (sh) nm(6,130).

IR (KBr pellet): 3423 (OH), 3098, 2944, 2672, 2523, 2486, 2362, 1726 (C=O), 1658, 1626, 1513, 1459, 1408, 1346, 1298, 1271, 1247, 1191, 1149, 1075, 992, 939, 919, 825, 816, 797, 783, 732, 723, 709, 646, and 617cm^{-1}.

^{1}H-NMR: 1.70 (s, broad, 4H), 3.12 (s, broad, 9H), 3.44 (s, broad, 2H), 4.15 (s, broad, 2H), 5.81 (d, 1H, J=10.26), 6.07(d.d, 1H, J=16.86, J=10.26), 6.36 (d, 1H, J=16.86), 7.08 (s, broad, 4H), 9.15 (t, 2H, J = 2.2 Hz), 9.20 (d, 4H, J = 2.2 Hz), and 9.39 (s, broad, 2H)ppm, Addition of D_2O caused the disappearance of the broad peak at 9.39ppm.

^{13}C-NMR: 22.39, 25.80, 41.78, 43.51, 55.31, 63.62, 117.00, 121.03, 128.12, 129.54, 130.92, 137.86, 139.10, 140.50, 148.29, 166.11, and 166.41ppm.

Found: C, 51.64; H, 4.59; N, 12.04%. $C_{30}H_{32}N_6O_{14}$ is C 51.43% , H 4.60%, N 12.00%

2.5.18 Synthesis of N-aryloyl-N-methyl-1-aminoanthraquinone (107)

N-Methyl-1-aminoanthraquinone (96) (2.37g, 0.01mol) and triethylamine (1.21g, 0.012mol, 20% excess) were dissolved in chloroform (50 cm^3), and acryloyl chloride (1.08g, 0.012mol, 20% excess) was then added slowly with stirring. After the completion of the addition of acryloyl chloride, the solution was heated under reflux until TLC showed the reaction was nearly completed (4 hours). The solution was cooled to room temperature and diluted with chloroform (50cm^3), then washed with water (2X80cm^3), and 0.2M hydrochloric acid (3X100cm^3). The chloroform solution was dried over magnesium sulphate. Removal of the solvent gave a solid (107) (1.31g, 45%). After three times recrystallization from toluene an analytically pure sample of (107) was obtained, m.p. 183 - 184 ^{o}C.

Infrared spectrum (KBr pellet): 3536, , 3067, 2929, 1671 (C=O), 1614, 1593, 1576, 1468, 1429, 1399, 1364, 1325, 1311, 1279, 1243, 1163, 1139, 1076, 981, 914, 851, 812, 791, 759, 745, 708, 687, 669, 638, and 622cm^{-1}.

^{1}H-NMR: δ 3.37 (s, 3H), 5.40 (d, 1H, J = 8 Hz), 5.36 (d d, 1H, J = 15.2 Hz, J = 8Hz), 6.51(d, 1H, J = 15.2 Hz), 7.61 (d, 1H, J = 5.2 Hz), 7.77 (m, 2 H), 7.86 (t, 1H, J = 5.2 Hz), 8.23 (m, 2H), and 8.42 (d, 1H, J = 5.2 Hz).

^{13}C-NMR: 36.54 (Me), 126.88, 127.55, 127.84, 127.98, 128.07, 129.02, 132.41, 134.10, 134.63, 134.82, 135.68, 136.55, 143.07 (aromatic C-N), 165.34(N-C=O), 181.99 (C-C=O), and 182.55 (C-C=O)ppm.

Found: C, 74.20; H, 4.54; N, 4.61%. $C_{18}H_{13}O_3N$ requirs C, 74.22; H, 4.50; N 4.81%.

It was sometimes found difficult to recrystallize the crude product, if any unreacted N-methyl-1-aminoanthraquinone (96) remained in the product. There were two ways to get rid of the starting material in this situation, one was to use more hydrochloric acid to wash the chloroform solution, another was to pass the product down a silica chromatography column with chloroform as the mobile phase. The first small fraction was N-methyl-1-aminoanthraquinone, the second big fraction was product (107).

2.5.19 Synthesis of 3-chloropropyl acrylate (110)

3-Chloropropanol (26.48g, 0.28mol) was added to a three necked round bottom flask to which hydroquinone (0.1g), and copper flakes (0.1g) had been added as inhibitors. Then acryloyl chloride (25.4g, 0.28mol) was added slowly with stirring and ice cooling. After the addition of the acryloyl chloride, a calcium chloride drying tube was fitted, and a N_2 inlet was used to remove hydrogen chloride being liberated from the reaction. After 7 hours refluxing at 65^{o}C, the mixture was distilled under vacuum. Two fractions were obtained.

Fraction 1 (b.p. 40 - 45^{o}C/1.5 m bar) was 3-chloropropyl acrylate (110) (11.78g, 28%).

IR (liquid film): 2962, 2915, 1722 (C=O), 1631(C=C), 1615, 1446, 1406, 1351, 1291, 1266, 1198, 1092, 1058, 1030, 985, 911, 995, 910, 788, 727, and 656cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ 2.12ppm (quintet, 2H, J = 6 Hz), 3.62ppm (t, 2H, J = 6 Hz), 4.30ppm (t, 2H, J = 6 Hz), and 5.5 - 6.5ppm (m, 3H).

Found: C, 48.09; H, 6.00%. $C_6H_9O_2Cl$ require C, 48.48; H, 6.06%.

Fraction 2 (b.p.74 - 80°C/1.5 mbar) was 3-chloro-propyl-β-chloro-propionate (112) (10.88g, 21%).

IR (liquid film): 2961, 1731(C=O), 1445, 1418, 1399, 1360, 1297, 1217, 1198, 1119, 1092, 1017, 933, 895, 782, 726, and 657cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ 2.12ppm (quintet, 2H, J = 6 Hz), 2.81ppm (t, 2H, J = 6.6 Hz), 3.62ppm (t, 2H, J = 6 Hz), 3.78ppm (t, 2H, J = 6.6 Hz), and 4.30ppm (t, 2H, J = 6 Hz)ppm.

Found: C, 38.64; H, 5.20%. $C_6H_{10}O_2Cl_2$ requires: C, 38.92; H, 5.41%.

2.5.20 Synthesis of 2-morpholinomethylhydroquinone (114)

A mixture of morpholine (113) (17.42g, 0.2mol) and paraformaldehyde (6.01g, 0.2mol) was heated on a water bath to achieve homogeneity. After cooling, the mixture was added to a solution of hydroquinone (110.11g, 0.25mol) in 400cm^3 acetone. At 20°C, the solution was stirred for 8 hours, then the solvent was evaporated off at 20°C under vacuum. Three recrystallizations of the resulting solid from ethyl acetate, followed by washing with chloroform after each recrystallisation, gave 2-morpholinomethylhydroquinone (114) (15.90g, 38%), m.p. 155 - 156°C (lit[118] 148 - 149 °C).

IR (KBr pellet): 3283 (OH), 2870, 1613, 1512, 1452, 1346, 1334, 1277, 1255, 1206, 1152, 1116, 1074, 1036, 1008, 987, 959, 931, 911, 880, 863, 823, 802, 774, 715, and 643 cm^{-1}.

^{1}H-NMR: δ 2.53ppm (s, 4H), 3.63ppm (s, 2H), 3.74ppm (s, 4H), 6.48ppm (d, 1H, J = 2.9 Hz), 6.62ppm (d.d, 1H, J = 8.4 Hz, J = 2.9 Hz), 6.66ppm (d, 1H, J = 8.4Hz), and 7.50 (s, broad, 2H)ppm.

^{13}C-NMR: 52.81, 61.66, 66.77, 115.50, 115.75, 116.61, 121.45, 148.76, and 150.62ppm.

Found: C, 63.62; H, 7.36; N, 6.69%. $C_{11}H_{15}NO_3$ requires: C, 63.14; H, 7.23; N 6.69%.

The chloroform washing were combined. Removal of the solvent gave a white powder. Three recrystallizations from ethyl acetate gave analytically pure 2,5-bis(morpholinomethyl)hydroquinone (116) (3.39g, 11%), m.p. 207.0-208.5^{o}C . Spectroscopic data are listed in the next subsection.

2.5.21 Synthesis of 2,5-bis(morpholinomethyl)hydroquinone (116)

2,5-Bis(morpholinomethyl)hydroquinone (116) could be readily obtained by adding twice the amount of morpholine and paraformaldehyde and reacting at 50^{o}C for 8 hours.

A mixture of morpholine (113) (34.84g, 0.4mol) and paraformaldehyde (12.02g, 0.4mol) was heated on a water bath to achieve homogeneity. the mixture was added to a solution with hydroquinone (110.11g, 0.25mol) in 400cm^3 acetone. At 50^{o}C, the solution was stirred for 8 hours, then the solvent was removed. Three recrystallizations of the resulting solid from ethyl acetate gave 2,5-bis(morpholinomethyl)hydroquinone (116) (49.96g, 81%), m.p. 207.0 - 208.5^{o}C (lit.[118] 203.0 - 205.0).

IR (KBr pellet): broad peak from 3500 - 2500, 2962, 2851, 1479, 1452, 1435, 1373, 1337, 1325, 1297, 1277, 1259, 1230, 1212, 1195, 1164, 1113, 1070, 1030, 1005, 985, 911, 886, 865, 826, 797, 753, 721, and 613cm^{-1}.

^{1}H-NMR: δ 2.55ppm (s, 8H), 3.65ppm (s, 4H), 3.75ppm (s, 8H), 6.5ppm (s, 2H), 10.05ppm (s, broad, 2H).

^{13}C-NMR: 52.906, 61.567, 66.782, 116.070, 120.841, 149.897ppm.

Found: C, 61.93; H, 7.81; N 8.97%. $C_{16}H_{24}N_2O_4$ requires: C, 62.32; H, 7.84; N 9.08%.

2.5.22 Synthesis of 2,5-bis(piperidinomethyl)hydroquinone (117)

Piperidine (4.45g, 0.052mol) and paraformaldehyde (1.57g, 0.052mol) were mixed slowly and then heated on a water bath to achieve homogeneity. After cooling, the mixture was added slowly to a solution of hydroquinone (2.86g, 0.026mol) in acetone (100cm^3). After 8 hours of stirring at room temperature, the solvent was removed giving a solid. Three recrystallizations from ethyl acetate gave white crystals of (117) (4.43g, 56%), m.p.188.0-189.0 ^{o}C .

IR (KBr pellet): Broad peak from 3500 - 2500 (OH), 2947, 2860, 2809, 1480, 1452, 1378, 1353, 1333, 1325, 1304, 1281, 1241, 1207, 1190, 1152, 1115, 1106, 1068, 1040, 988, 962, 907, 870, 827, 808, 786, 751, and 646cm^{-1}.

^{1}H-NMR: δ 1.45 (s, broad, 4H), 1.59 (quintet, 8H, J = 5.6 Hz), 2.48 (s, broad, 8H), 3.58 (s, 4H), 6.43 (s, 2H), and 10.10 (s, broad, 2H)ppm.

^{13}C-NMR: 24.02, 25.88, 53.89, 61.94, 115.59, 121.26, and 150.14ppm.

Found: C, 71.20; H, 9.31; N, 8.98% . $C_{18}H_{28}N_2O_2$ requires: C, 71.02; H, 9.27; N 9.20%.

2.5.23 Attempted reactions with 2-morpholinomethylhydroquinone (114)

(a) Reaction with acrylic acid

2-Morpholinomethylhydroquinone (114) (10.46g, 0.05mol), acrylic acid (3.60g, 0.05mol) and toluene (50cm^3) were placed in a flask then heated at 50^{o}C for five hours. After cooling down a sticky substance formed on the bottom of the flask. The toluene solution was decanted, the sticky substance was left in the flask. Addition of aqueous sodium hydroxide solution (1M, 50cm^3) in the flask gave a solid. This solid was isolated and checked with IR and ^{1}H-NMR. The spectra of this solid were identical to those of (114). Therefore it was confirmed that the sticky substance formed in the solution was the salt of (114) with acrylic acid.

(b) Reaction with acetic acid

2-Morpholinomethylhydroquinone (114) (10.46g, 0.05mol), acetic acid (3.0g, 0.05mol), concentrated sulphuric acid (5cm^3) and toluene (100cm^3) were placed in a flask then heated at 110^{o}C under nitrogen for four hours. After cooling down a sticky substance formed on the bottom of the flask. The sticky substance was collected. Addition of aqueous sodium hydroxide solution into the sticky substance gave a solid. This solid was isolated and checked with IR and TLC. The IR spectrum of this solid and TLC spot were identical to those of (114). Therefore it was confirmed that the sticky substance formed in the solution was a salt of (114).

(c) Reaction with acetyl chloride then with acetic acid

2-Morpholinomethylhydroquinone (114) (10.46g, 0.05mol) was dissolved in THF (200cm^3) at room temperature. Then acetyl chloride (3.93g, 0.05mol) was added in the solution dropwise. A white precipitate formed immediately. After 20 minutes stirring at room temperature, white precipitate was collected by suction filtration. This white precipitate was used directly in the next stage reaction without further purification.

The white solid obtained from the first stage, acetic acid (3.3, 0.05mol) and toluene ($100cm^3$) were placed in a flask then heated to 100^oC under nitrogen. The white solid was dissolved slowly. After four hours stirring at 100^oC the solution was cooled and a sticky substance formed on the bottom of the flask which was confirmed being a salt of (114). Compound (114) was isolated by adding aqueous sodium hydroxide solution into the salt.

(d) Reaction with iodomethane then with acetic acid

2-Morpholinomethylhydroquinone (114) (10.46g, 0.05mol) was dissolved in THF ($20cm^3$) at room temperature. Then iodomethane (7.1g, 0.05mol) was added in the solution. Temperature was obtained at 40^oC carefully for 30 hours with stirring. After cooling down, a crystal formed in the flask. This crystal (16.0g, 87%) was used directly in the next step synthesis without further purification.

The crystal obtained from the first stage (16.0g), acetic acid (3.3, 0.05mol) and toluene ($100cm^3$) were placed in a flask then heated to 100^oC under the protection of nitrogen. After 20 hours stirring at 100^oC the solution was cooled and a sticky substance formed on the bottom of the flask which was found to be a salt of (114). Compound (114) was isolated by adding aqueous sodium hydroxide solution into the salt.

Chapter III

Synthesis and characterization of electroactive polymers

3.1 Introduction

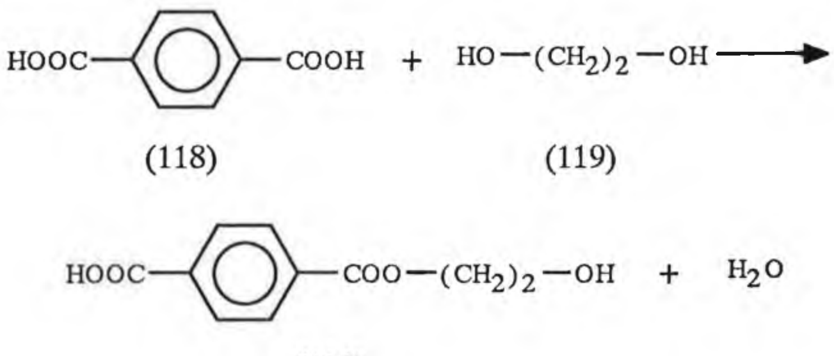
The monomers whose synthesis was discussed in the previous chapter were polymerized to give homopolymers and copolymers. The synthesis and characterisation of these polymers are reported in this chapter.

It is conventional to divide the synthesis of polymers into two main categories. One is step-growth polymerization (often called condensation polymerization since it is almost exclusively concerned with condensation reactions taking place between multifunctional monomer molecules with elimination of a small molecule) and the other category is addition polymerization where the monomer molecules add on to a growing chain one at a time and no small molecules are eliminated during the reaction.

3.1.1 Step-growth polymerization

Step-growth polymerization is characterized by the gradual formation of polymer chains through successive reactions coupling monomers to each other to form dimers which can also react with other dimers or unreacted monomer molecules.[119]

Since step-growth polymerization is mainly concerned with condensation reactions, small molecules are almost always produced by the reaction. In order to produce polymer molecules by step-growth polymerization it is essential that the monomer molecules must be able to react at two or more sites. A typical condensation reaction is: a diacid (118) and a diol (119) reacted to yield an ester (120) which still has unreacted end groups.



(118) (119) (120)

The ester (120) produced has an acid group at one end and a hydroxyl group at the other and so can react with other monomer or "dimer" molecules to form a "trimer" or "tetramer" and go on through further condensation reactions to form long polymer molecules. The number of sites at which a monomer molecule is able to react is called its functionality and this is a concept which is of prime importance in step-growth polymerization. In order to form linear molecules it is necessary that the monomer molecules are bifunctional. If the monomer has a functionality of greater than two it is usually possible to form branched network polymers rather than linear molecules.

There are two main factors which may affect the formation of high molecular weight polymers. One is that an equimolar mixture (i.e. equal numbers of reacting functional groups) should be used otherwise the molecular weight of the polymer will be low. For example in the reaction above if there is an excess of diacid (118), intermediate short polymer molecules are produced which have acid end groups. Another factor which can tend to reduce the yield of high molecular weight polymer molecules, even when equal numbers of functional groups are employed, is the equilibrium which occurs between the reactants and products during condensation reactions. If the concentration of the condensate is allowed to build up, the reaction may stop and can even be forced in the reverse direction. This problem is usually readily overcome by removing the condensate as it forms and so driving the reaction in the forward direction.

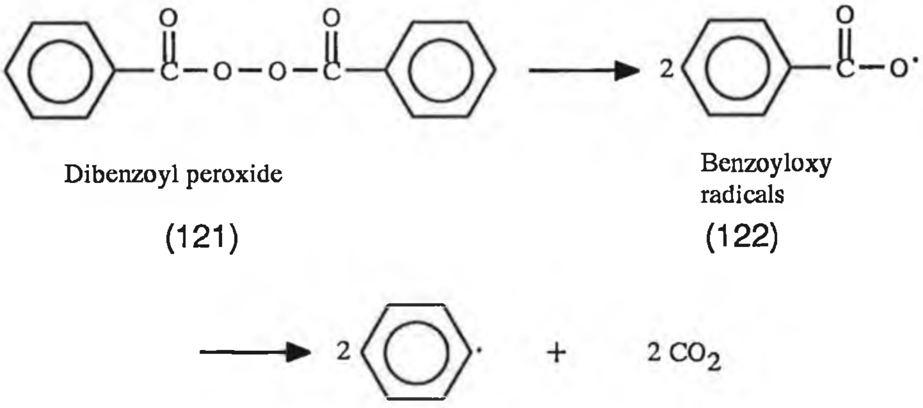
3.1.2 Addition polymerization

Addition polymerization is the second main type of polymerization reaction. It differs from step-growth polymerization in several important ways. It takes place in three distinct steps, initiation, propagation and termination and the principal mechanism of polymer formation is by addition of monomer molecules to a growing reactive intermediate. Monomers for addition polymerization normally contain double bonds and are of the general formula $CH_2{=}CR_1R_2$. The double bond is susceptible to attack by either free radical or ionic initiators to form a species known as an active centre. This active centre propagates a growing chain by the addition of monomer molecules and the active centre is eventually neutralized by a termination reaction. Since the reaction only occurs at the reactive end of the growing chain long molecules are present at an early stage in the reaction along with unreacted monomer molecules which are present until very near the end of the reaction. It is possible to generalize about many features of addition polymerization, but there are sufficient differences between free radical and ionic initiated reactions for the two types to be treated separately.

3.1.2.1 Free radical initiation

Free radicals are species which contain an unpaired electron. They are extremely reactive and will react with monomers containing a double bond to form an active centre which is capable of reacting with further monomer molecules to give a growing molecular chain. In order for an initiator molecule to be effective it must be capable of breaking down into radicals which are stable long enough to react with a monomer molecule and form an active centre. Initiators are normally required to form radicals in a controlled way under mild conditions, usually by the application of heat or electromagnetic radiation.[120]

Free radicals may be readily produced by thermal decomposition of certain peroxides and azo compounds. Dibenzoyl peroxide (121) breaks down to give benzoyloxy radicals (122) which in turn break down to phenyl radicals (123) and carbon dioxide.



Dibenzoyl peroxide

(121)

Benzoyloxy radicals

(122)

Phenyl radicals

(123)

Azo compounds decompose both by the application of heat and by photolysis. For example, azobisisobutyronitrile (124) breaks down into cyanopropyl radicals (125) and nitrogen at ambient temperature under the action of ultra-violet radiation.

$$\underset{CN}{Me_2C}-N{=}N-\underset{CN}{CMe_2} \longrightarrow 2\ \underset{CN}{Me_2C}\cdot + N_2$$

Azobisisobutyronitrile

(124)

Cyanopropyl radicals

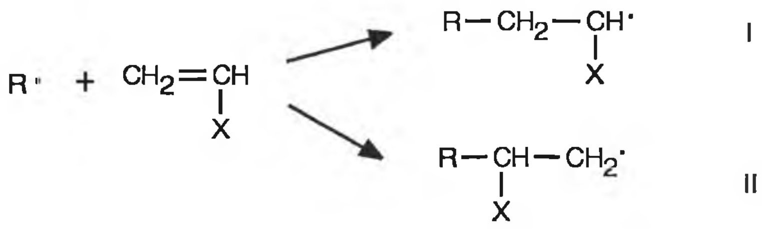
(125)

Redox reactions may be used to produce radicals and they are particularly useful for the initiation of polymerization at low temperatures or for emulsion polymerization in aqueous systems. The reaction between hydrogen peroxide

(127) and the ferrous ion (126) produces ferric ions (128) and hydroxyl radicals (129) in solution:

$$\underset{(126)}{Fe^{2+}} + \underset{(127)}{HOOH} \longrightarrow \underset{(128)}{Fe^{3+}} + \underset{(129)}{HO\cdot} + OH^{-}$$

Once the initial free radicals have been formed the next stage of the initiation process is the formation of an active centre or chain carrier. Very often the monomer is a vinyl molecule of general formula $CH_2{=}CHX$. There are two possible reactions:

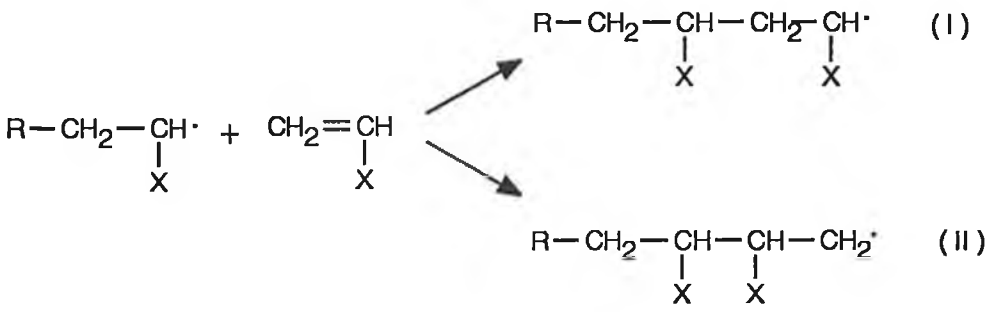


The relative amounts of the two possible product radicals (I and II) depend upon the difference between the activation energies for the two reactions. The activation energy for formation of II is slightly higher than that for I because the X group which is usually large and bulky tends to hinder the approach of the R· radical to the substituted end of the double bond. Additionally, I has the substitutent in position to stabilize the free radical by resonance or induction, while II has no effects of this kind. Consequently, the initiation step strongly favors the formation of $R\text{-}CH_2\text{-}CHX\cdot$ radical (I).

3.1.2.2 Propagation

Chain propagation takes place by the rapid addition of monomer molecules to the growing chain. The average life-times of the intermediate radicals are extremely short and several thousand additions can take place within a few seconds.

As with the reaction between the radical and first monomer molecule described before there is the problem of the way that the monomer adds on. There are two possibilities again for the way in which addition can take place:



The first type of addition (I) is known as " head-to-tail" addition and the second kind is called "head-to-head". The possibility of the "head-to-tail" and " head-to-head" addition in the polymerization is dependent on two processes:

1. The relative energy requirements of the transitions states.

2. The relative stabilities of the products

The "head-to-tail" addition is favored by both processes. That is, the steric requirements in the transition states are lessened, since the substitutent is one carbon removed from the attacking species. Additionally, the "head-to-tail" product has the substitutent in position to stabilize the product by resonance or induction. Therefore, the propagating step proceeds predominantly by head-to-tail polymerization.

3.1.2.3 Termination

Free radicals are particularly reactive species and there are several ways in which the growing chains can react to form inert covalently bonded polymer molecules. The most important mechanisms of termination are when two growing chains interact with each other and become mutually terminated by one of two specific reactions. One of these reactions is combination, where the two growing chains join together to form a single polymer molecule:

$$\sim CH_2-\underset{X}{CH}\cdot + \cdot\underset{X}{CH}-CH_2\sim \longrightarrow \sim CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2\sim$$

The combination results in a "head-to-head" linkage. Alternatively a hydrogen atom can be transferred from one chain to the other in a reaction known as disproportionation:

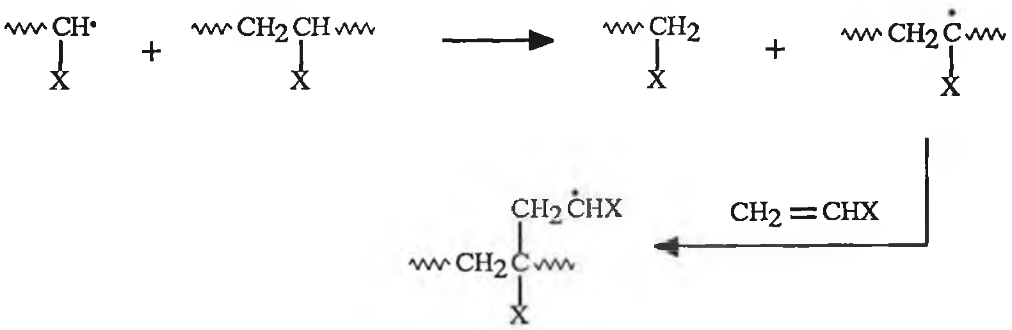
$$\sim CH_2-\underset{X}{CH}\cdot + \cdot\underset{X}{CH}-CH_2\sim \longrightarrow \sim CH_2-\underset{X}{CH_2} + \underset{X}{CH}=CH\sim$$

The growing chains become two polymer chains, one with a saturated group at the end and the other with an unsaturated group at its end. Also these chains have an initiator fragment at only one end whereas polymer molecules formed by combination termination reactions have initiator fragments at both ends.

In general it is found that both types of termination take place in any particular system but to different extents. For instance, it is found that polystyrene terminates principally by combination whereas poly(methyl methacrylate) terminates almost exclusively by disproportionation at high temperature and by both processes at lower temperature.[121]

The other main mechanism of termination is by chain transfer which can take place in a number of different ways. It is a process whereby a chain stops growing but the polymerization process does not stop.

The radical chain can transfer to a polymer resulting in branching of the polymer chain.



It can also transfer to monomer, initiator or a solvent molecule. Because the radical chain can transfer to a solvent, and often large numbers of solvent molecules are present in the polymerization system, the selection of a suitable solvent for a polymerization is very important. For example, in the polymerisation of styrene in carbon tetrachloride, due to transferring of free radical to solvent, the polymer produced contains chlorine at the chain ends (fig. 3.1).

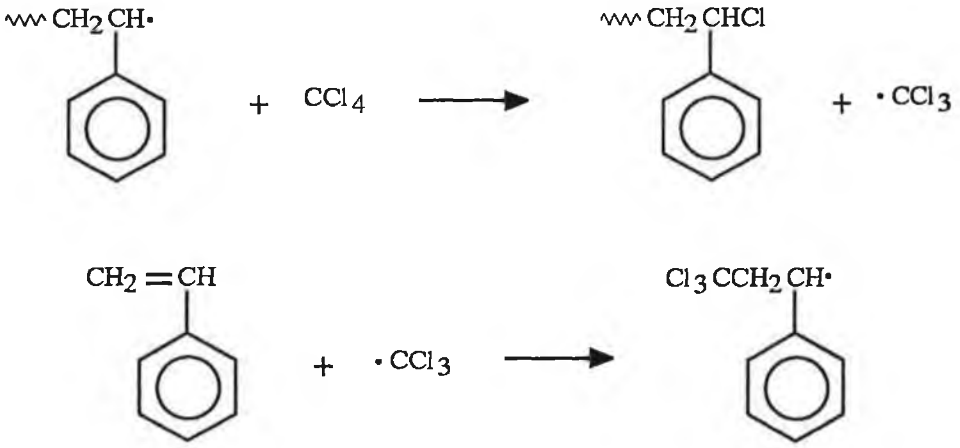


Figure 3.1

3.1.2.4 Ionic polymerization

Ionic polymerizations[122] are classified according to whether the polymeric ions are positively or negatively charged. If the ions are positively charged the polymerization is termed cationic and if they are negatively charged it is known as anionic polymerization. Figure 3.2 illustrated the cationic polymerisation of styrene initiated with perchloric acid.

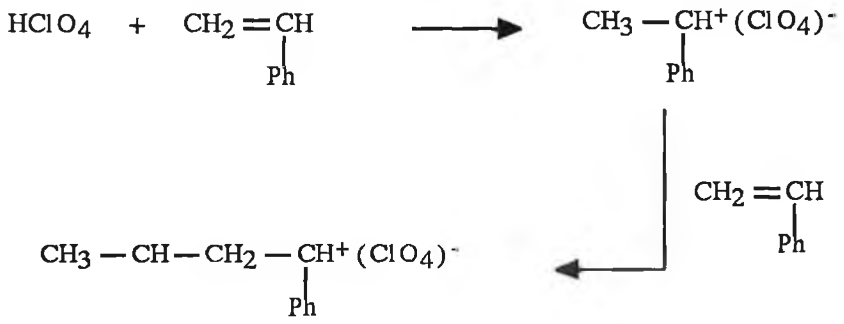


Figure 3.2

Figure 3.3 shows an example of anionic polymerisation of styrene initiated by potassium amide.

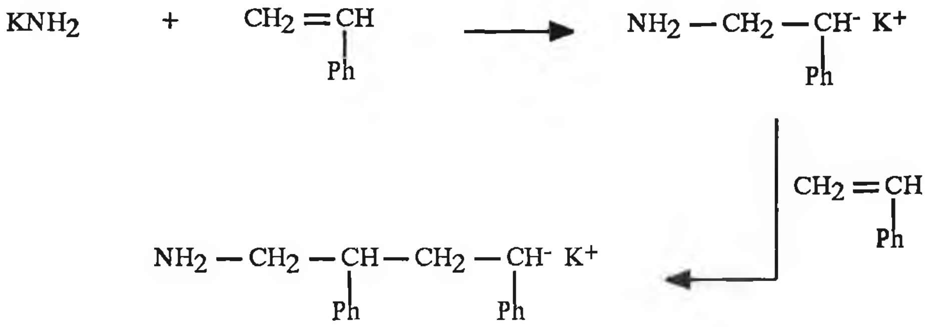


Figure 3.3

It is normally possible to generalize about the mechanisms and kinetics of free-radical addition polymerization, but in the case of ionic initiated polymerization such generalizations cannot normally be made since unlike free radical systems, the detailed mechanisms depend upon the type of initiator, monomer and solvent employed. When the chain carriers are ionic the addition reactions are often rapid and difficult to reproduce. High rates and degrees of polymerization can be obtained at low temperature. Propagation rarely takes place through free ions. Normally there are counter ions closely associated with the polymer ions during chain propagation. The nature of the solvent influences the strength of the association and the distance between the ions in the ion-pair. The presence of the counter ion, in turn, can control the stereochemistry and the rate of monomer addition[122]

Ionic polymerization systems have been developed because some monomers which contain double bonds cannot be polymerized using free-radical initiators. Also ionic polymerization generally takes place at low temperatures and can offer better control of stereoregularity and relative molecular mass distribution. The chemical factors which control whether or not a particular monomer can be polymerized using free radical, cationic or anionic initiators rely on the properties of the substitutent groups. If the substitutent group is a strong electron withdrawing group, the monomer can be initiated by an anionic initiator. If the substitutent group is a strong electron donating group, the monomer can be initiated by a cationic initiator. In general free radicals are less selective and can polymerize most types of monomers.

3.1.2.5 Ziegler-Natta polymerisation

During experiments in the 1950s on the polymerisation of ethylene using organometallic catalysts in inert atmospheres, Ziegler discovered that it was possible to make a linear form of polyethylene which was highly crystalline in contrast to the low crystallinity branched form prepared by conventional high-pressure polymerisation.[123] Subsequently Natta showed that similar catalysts could be used to polymerise α-olefins such as 1-butene or propylene which could not be polymerised using conventional free radical or ionic initiators.[104] The polymers produced using these catalysts can also possess a high degree of stereoregularity and Ziegler-Natta catalysts are now extremely important as commercial catalysts for the production of linear polyethylene and isotactic polypropylene.

A typical catalyst combination for the polymerisation of propylene is triethyl aluminium and titanium chloride. The mechanisms and kinetics of Ziegler-Natta polymerisation are known to be complex and are not yet fully understood. It is clear that the reaction takes place at the surface of the solid catalyst and that there is some type of complex formed at the surface. It is thought that the stereoregulation occurs from the way in which the monomer molecules are oriented during addition to the growing chain at the catalyst surface, although there is still considerable argument over the exact way in which this occurs.

3.1.2.6 Group transfer polymerisation

Of the various vinyl polymerization methodologies, that of group transfer polymerisation has arrived on the scene most recently.[125-127] Its commercial potential and basic chemistry are the subject of intense investigation.

The group transfer polymerisation method converts monomers frequently used in anionic polymerisation into living polymers; however, the propagating chain is covalent in character. Typically, an organosilicon compound is used to initiate the polymerisation in solution in the presence of an anionic or lewis acid catalyst. The process is illustrated in figure 3.4 for the polymerisation of methyl methacrylate using the methyl trimethylsilyl acetal of dimethylketene as initiator and bifluoride ion as catalyst. In each propagation step the $SiMe_3$ group is transferred to the carbonyl oxygen of the incoming monomer, hence the name group transfer polymerisation.[128]

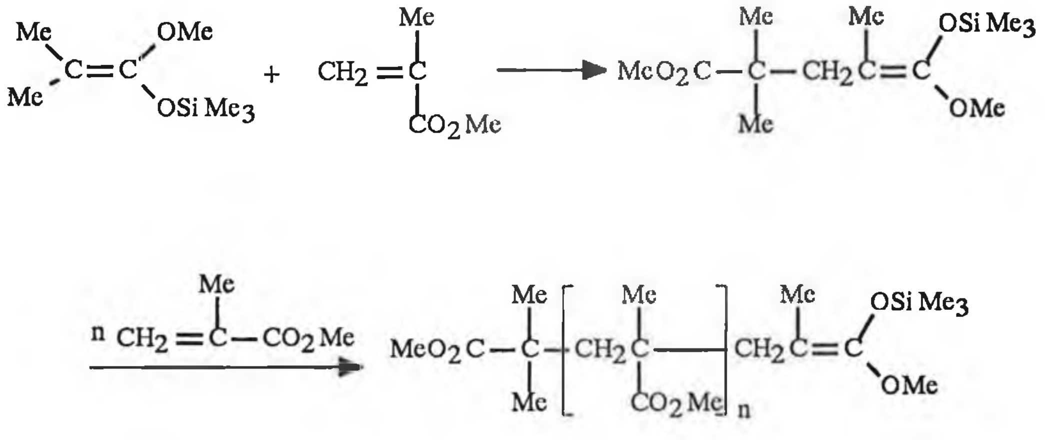


Figure 3.4

3.1.2.7 Copolymerization

It is a common practice in materials science to improve the properties of one material by mixing it in some way with another material. Metal alloys have mechanical properties which are often vastly superior to those of pure metals. In polymer science, both physical "mixing" (blending) and chemical "mixing" (copolymerizing) have been used to modify the properties of polymeric materials. Many polymers cannot be blended or mixed satisfactorily and the properties of the blend are often inferior to those of the pure polymers. However, chemical "mixing" to synthesize polymers which have more than one type of monomer unit in the polymer chain can give properties which may be better than those of the parent homopolymers. The properties of the copolymer are usually characterized by the detailed arrangements of the monomer units on the polymer chain. The simplest types of copolymer contain only two types of monomer unit and there are several ways in which they can be arranged in the macromolecules.

Random copolymers are formed where there is a random sequence of the two monomer units (A and B) along the polymer:

—A—B—B—B—A—B—A—B—B—B—A—A—

In alternating copolymers the two kinds of monomer occur alternately along the polymer chain.

—A—B—A—B—A—B—A—B—A—B—A—B—

Block copolymers contain long sequences of each monomer separately in a linear copolymer. Some times the block copolymer is made up of just two or three long blocks of each type of unit giving a material with interesting and unusual properties.

—A—A—A—A—A—A—A—B—B—B—B—B—B—A—A—A—A—A—

The last main type of copolymer that is usually considered is grafted copolymers. They consist of a main homopolymer chain with branches of another type of homopolymer.

In general it is found that block and graft copolymers have properties characteristic of both the homopolymers whereas alternating and random copolymers possess properties somewhere between those of the two homopolymers.

It is clear that copolymerization is a much more complex process than polymerization using a single monomer. For example, in addition copolymerization using two monomers the tendency of each type of monomer to add to the growing chain may be different. This can lead to a variation of copolymer composition during the reaction even when equimolar amounts of the two types of monomer are used initially. This phenomenon is known as composition drift and is a common feature in copolymerization reactions.

3.1.3 Molecular weight and molecular weight distribution[129]

Molecular weight is an extremely important variable because it relates directly to a polymer's physical properties. In general, the higher the molecular weight, the tougher the polymer. However, too high a molecular weight can lead to processing difficulties.

Techniques available for determining molecular weights of polymers include osmometry, light scattering, ultracentrifugation, end group analysis, ebulliometry, cryoscopy, viscometry and Gel Permeation Chromatography (GPC). Molecular weight values obtained depend in large measure on the method of measurement.

The number average molecular weight ($\overline{M}_n$) is defined as the total weight of all solute species divided by the total number of moles present:

$$\overline{M}_n = \Sigma N_i M_i / \Sigma N_i$$

where N_i is the number of moles of solute of species i, M_i is the molecular weight of species i, $N_i M_i$ is the actual weight of species i. The number-average molecular weight is highly sensitive to the presence of a small number fraction of low-molecular weight macromolecules. It can be obtained from membrane osmometry, ebulliometry, cryoscopy, and end-group analysis, which are all dependent on the number of molecules present.

The weight-average molecular weight ($\overline{M}_w$) is defined as:

$$\overline{M}_w = \Sigma N_i M_i^2 / \Sigma N_i M_i$$

It is highly sensitive to the presence of small amounts by weight of high-molecular weight macromolecules and can be obtained from light scattering and ultracentrifugation, which are dependent on the weight of solute present.

The Z-average molecular weight (M_Z) is defined as:

$$M_Z = \Sigma N_i M_i^3 / \Sigma N_i M_i^2$$

Its physical meaning is not clear, and it is only an average value obtained from ultracentrifugation.

Viscosity-average molecular weight (M_V) can be related to intrinsic viscosity ([η]) by the Mark-Houwink-Sakurada equation:

$$[\eta] = KM_V^{\alpha}$$

The constants K and α are the intercept and slope, respectively, of a plot of log [η] versus logM_W or logM_n of a series of fractionated polymer samples. Such plots are linear (except at low molecular weights) for linear polymers, thus

$$\log[\eta] = \log K + \alpha \log M$$

The viscosity-average molecular weight (M_V) is defined as:

$$M_V = [\, \Sigma N_i M_i^{\alpha+1} / \Sigma N_i M_i \,]^{1/\alpha}$$

If $\alpha = 1$, then $M_V = M_W$.

The viscosity-average molecular weight (M_V) can be obtained only from viscosity measurements.

Between the different molecular weight averages the following relationship can be observed:

$$\overline{M}_n < \overline{M}_v < \overline{M}_w < \overline{M}_z$$

Molecular weight distribution is an important characteristic of polymers because, like molecular weight, it can significantly affect polymer properties. Just as low-molecular-weight polystyrene behaves differently from the high-molecular-weight material, a sample of polystyrene having a narrow molecular weight range will exhibit different properties from one having a broad range, even if the everage molecular weight of the two samples are the same. Broadly speaking, techniques for determining molecular weight distribution involve fractionation of the polymer sample and comparison of the fractions thus obtained with samples of known absolute molecular weight by means of some calibration procedure.

A single number or index has been used to describe the molecular weight distribution of a polymer. The polydispersity index is defined as $\overline{M}_w/\overline{M}_n$. In light scattering measurement, the larger molecules contribute more because they scatter light more effectively. It is for this reason that weight average molecular weights are always greater than number average molecular weights except, of course, when all molecules are of the same weight; then $\overline{M}_w = \overline{M}_n$. The narrower the molecular weight range, the closer are the values of $\overline{M}_w$ and $\overline{M}_n$, and the ratio $\overline{M}_w / \overline{M}_n$ may thus be used as an indication of the breadth of the molecular weight range in a polymer sample. If polydispersity index $\overline{M}_w / \overline{M}_n = 1$, the polymers all have the same molecular weight. If polydispersity index value is small, for example 2 or 3, the polymer have a narrow molecular weight distribution. The greater the polydispersity index is, the broader the molecular distribution of the polymer is.

3.1.4 Gel permeation Chromatography (GPC)

Gel Permeation Chromatography (GPC)[130] is the method used in the determination of molecular weights and molecular weight weight distributions in this thesis. GPC is used most widely as an analytical technique for determining the molecular weight and molecular weight distribution of a synthetic polymer sample. In GPC the columns are packed with porous particles, and the separation occurs because molecules of different size penetrate the pores of the stationary phase to various degrees. The method is somewhat like a reverse sieving operation at the molecular level. The largest molecules are excluded from the pores to the greatest extent and, hence, are the first to emerge from the column. Progressively smaller molecules permeate the porous stationary phase to increasing extents and are eluted sequentially. The eluted material is monitored for solute by a suitable detector, and an instrumental trace of the detector output provides distinct peaks for well-resolved mixtures and broad peaks for a continuous distribution of molecular sizes. With suitable calibration, this can be translated into a quantitative characterization of the sample.

A typical gel permeation chromatogram plots detector response against the volume of dilute polymer solution that passes through the column. To obtain molecular weights at a given retention volume, the chromatogram may be compared with a reference chromatogram obtained with fractions of known average molecular weight in the same solvent and at the same temperature. For purposes of comparson, the elution band is divided into "counts" of a specific volume, usually 2.5 or 5.0cm^3, with the height above the baseline being proportional to the amount of polymer eluted.

The major problem with calibrating a particular GPC column for a particular polymer is that few standard samples of narrow molecular weight distribution are available commercially. Polystyrene standards having polydisperity indexes close to unity are available over a wide range of molecular weights (600-2,500,000) and these are often used; if one is dealing with a polymer other than polystyrene, however, the molecular weights thus obtained are at best approximate and may in some instances be seriously in error. To circumvent this difficulty, the universal calibration method is employed.

The universal calibration method is based on the observation[131,132] that the product of intrinsic viscosity ($[\eta]$) and molecular weight (M) is independent of polymer type. This product, $[\eta]M$, is called the universal calibration parameter. For example, a plot of $\log([\eta]M)$ versus elution volume in tetrahydrofuran (THF) solvent yields a single curve, approximately linear, for a widely disparate group of polymers.[132] Thus $\log([\eta]M)$ may be considered a constant for all polymers for a given column, temperature, and elution volume. If we assume that the reference polymer (e.g., polystyrene) is polymer 1 and the polymer to be measured is polymer 2, it follows that

$$[\eta]_1 M_1 = [\eta]_2 M_2$$

From the Mark-Houwink-Sakurada relationship,[132]

$$[\eta]_1 = K_1 M_1^{\alpha_1}$$

$$[\eta]_2 = K_2 M_2^{\alpha_2}$$

The constant K and α are the intercept and slope, respectively, of a plot of $\log[\eta]$ versus $\log M_w$ or $\log M_n$ of a series of fractionated polymer samples. Such plots are linear (except at low molecular weights) for linear polymers

Combining these equations and solving for $\log M_2$, we obtain

$$\log M_2 = [1/(1+\alpha_2)]\log(K_1/K_2) + [(1+\alpha_1)/(1+\alpha_2)]\log M_1$$

To determine the molecular weight (M_2) at a given retention volume, the column must first be calibrated with the standard polystyrene fractions (same solvent, same temperature). This gives a relationship of the type shown in figure 3.5. Such semilogarithmic calibration plots are generally linear over a broad range of molecular weights, with deviation from linearity occurring at high and low molecular weights. K and α are constant, their values for common polymers are normally obtainable from a polymer handbook.[132, 133] However, for our new polymers, K and α were only estimated using the values of the calibration polymers. Substituting the value of M_1 for a particular retention volume from the calibration plot and the values of K and α in the above equation, M_2 can be readily calculated. GPC thus provides a rapid and convenient method of obtaining molecular weight distribution once the appropriate calibrations have been worked out.[132]

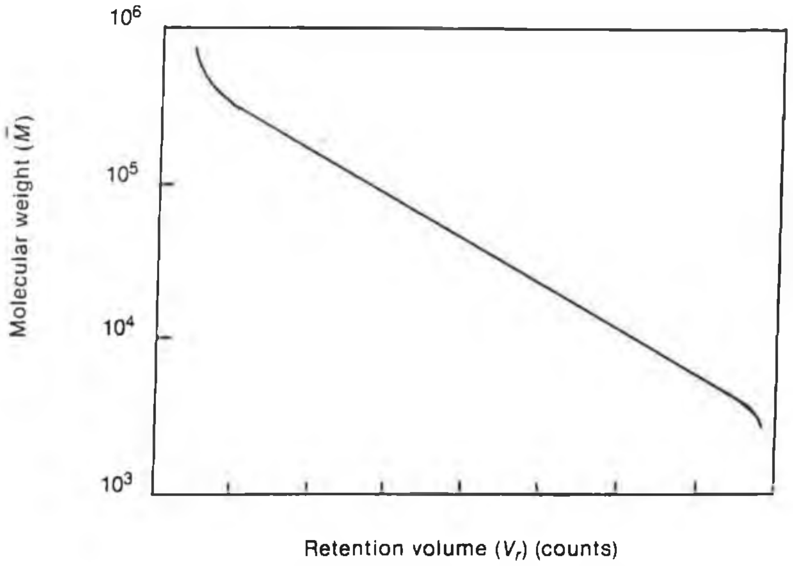


Figure 3.5 Typical semilogarithmic calibration plot of molecular weight versus retention volume

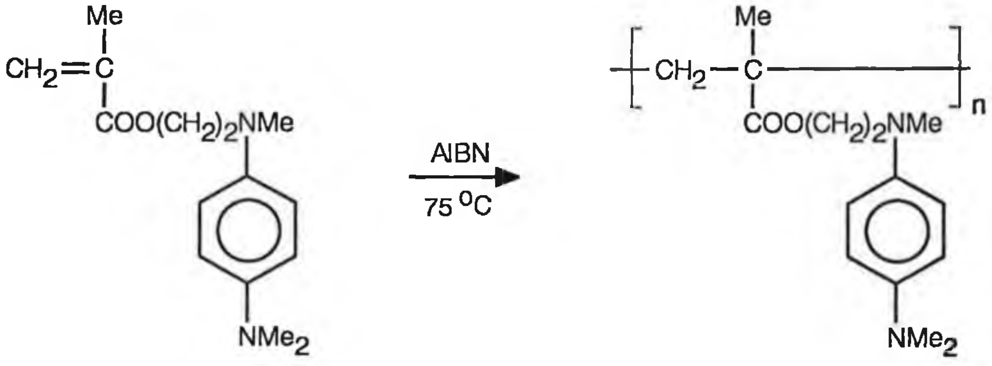
3.2 Results and discussion

3.2.1 Synthesis and characterisation of poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130)

The monomers whose synthesis was reported in Chapter II are acrylates and methacrylates and it was anticipated that they could be polymerised by both anionic and free radical initiators since both free radical and anionic polymerisation has been reported for the polymerization of methyl acrylate,[134] and methyl methacrylate.[135] The poly(methyl methacrylate) obtained from anionic polymerization is highly stereoregular, while the product from free radical polymerization is only atactic.[136] The anionic initiators investigated were sodium naphthalene and ethyl magnesium bromide. Both initiators have been reported working for the polymerization of methyl methacrylate.[136] However our attempts to polymerize 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98) with sodium naphthalene and ethyl magnesium bromide were not successful. The presence of trace base (or acid) in the monomer (98) could be the reason for the failed polymerisations. The monomer (98) was liberated from its toluenesulphonic acid salt (99) by addition of aqueous sodium hydroxide, and was then extracted with diethyl ether. Although the ether solution was washed with water and dried, trace amounts of base (or acid) may have remained in the monomer solution. Both base and acid are both inhibitors of anionic polymerization[122].The requirement for purity of a monomer in an anionic polymerization is extremely high. Because of the inability to rigourously purify the liberated monomers (high boiling point and susceptibility of the liquid monomers to atmospheric oxidation), no further efforts at anionic initiation were made.

For the free radical polymerizations, AIBN was used as the initiator and a number of solvents were investigated. Use of chloroform or ethanol did not yield any polymer. However ethyl acetate was found to be a suitable solvent for the AIBN initiated polymerization of 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98). Before polymerization, the monomer (98) was liberated from (99) by treatment with aqueous sodium hydroxide, and extracted into ethyl acetate. AIBN is one of the most commonly used initiators in free radical polymerization. It's rate of decomposition at 75^{o}C is quite fast, half life is about 5 hours.[120] The free radical polymerization of methacrylate and acrylate esters are markedly inhibited by oxygen,[137] therefore, considerable care was taken to exclude air during the polymerization stage.

After 7 hours polymerization under the protection of N_2, a viscous solution was obtained.



(98) (130)

The polymer (130) was purified by repeated precipitation by adding ethyl acetate solution in light petroleum (b.p. 40-60^{o}C).

GPC measurement showed that the molecular weight of this polymer (130) was quite high, $\bar{M}_n$ = 17,500, corresponding to an average of approximately 65 repeat units per polymer molecule (130). Molecular weight distribution is narrow as well, $\bar{M}_w/\bar{M}_n = 3.08$.

The IR spectrum of the product as expected showed the absence of a carbon-carbon double bond stretch at $1631 cm^{-1}$, present in the monomer (98). The

^{1}H-NMR spectrum (fig. 3.6) of the product (130) was also consistent with polymerisation having occurred. There were no vinyl protons present, instead two additional proton absorptions appeared in the aliphatic range.

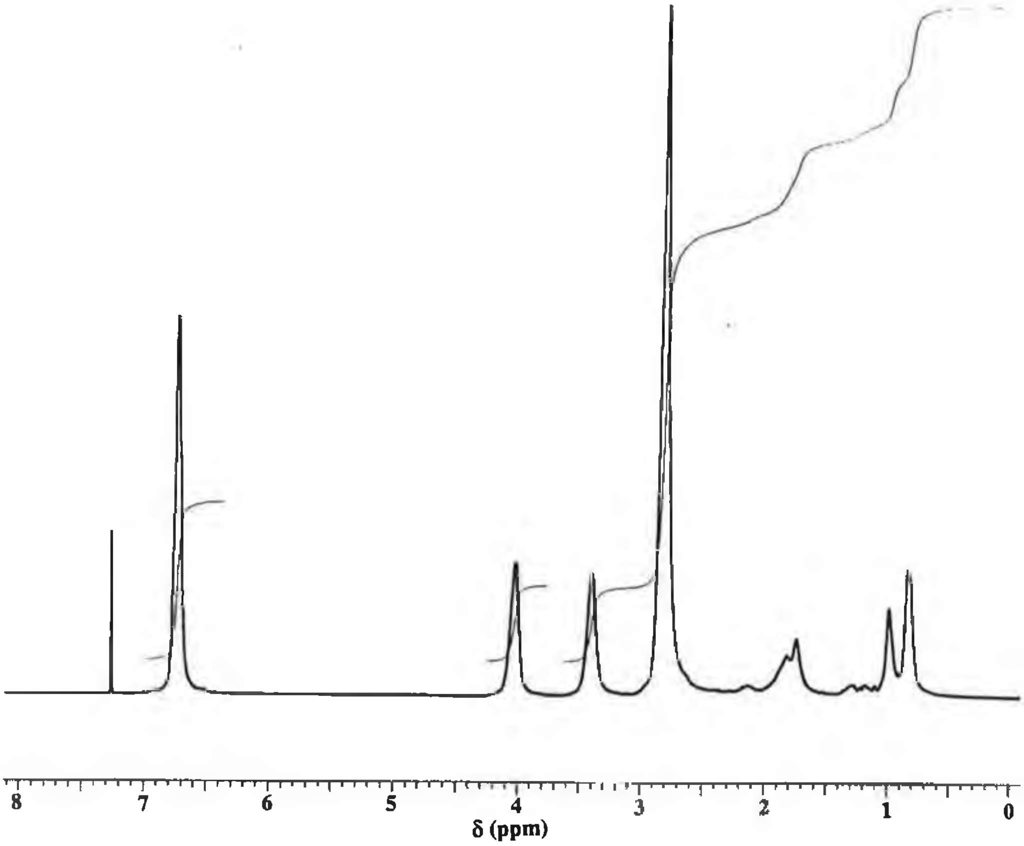
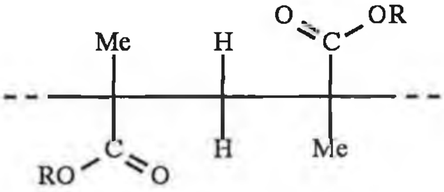


Figure 3.6 ^{1}H-NMR spectrum of poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130) ($CDCl_3$, Bruker ACF-400)

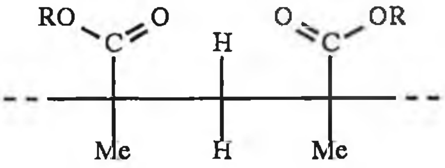
The assignment of this spectrum is quite interesting. The singlet at 6.77ppm represents the four aromatic protons, confirmed by the C-H correlation spectrum in which this peak correlated with two tertiary carbon peaks in the ^{13}C-NMR spectrum. The two singlets at 4.02ppm and 3.40ppm are assigned to the methylene protons connected to oxygen and nitrogen respectively. This was confirmed by a COSY spectrum, the peak at 4.02ppm being coupled to the peak at 3.40ppm, confirming their proximity to each other. The nine proton singlet at 2.80ppm is assigned to the three N-methyl groups. In the C-H correlation spectrum, this peak is correlated with two different primary carbons as expected. The assignment of peaks in ranges 0.6 - 1.4ppm and 1.5 - 2.2ppm are particularly relevant. Integration for the range 0.6 - 1.4ppm showed three protons. In this range there are two major peaks at 0.85 and 1.00ppm and two smaller peaks at 1.2 and 1.3ppm, slightly overlapped. The protons giving rise to this range of absorptions are those of the C-methyl groups. The situation in the range 1.5 - 2.2ppm is similar, integration for this range being for two protons. Three peaks can be seen in this range, two major ones at 1.75 and 1.83ppm, and a minor one at 2.1ppm. These peaks are assigned to the methylene protons of the polymer backbone. The multiole nature of these methyl and methylene absorption is related to differing stereochemical environments along the polymer backbone. Before further discussion of the NMR spectra of this polymer, it is helpful to rewiew detailed NMR studies of poly(methyl methacrylate) (PMMA).

The first information concerning the stereoregularity of polymers observed by NMR was from PMMA.[138] Since then NMR has found significant applications in polymer science, and results obtained have completely revolutionized thinking concerning isomerism and have led to an understanding of the stereochemical aspects of polymerization mechanisms.

PMMA is a most convenient starting point, since no vicinal coupling by the main chain protons complicates the spectrum. To interpret the PMMA NMR spectrum, let us consider the chain in terms of sequences of two monomer units or dyads. There are two possible types of dyads and they have different symmetry properties.



(a) r

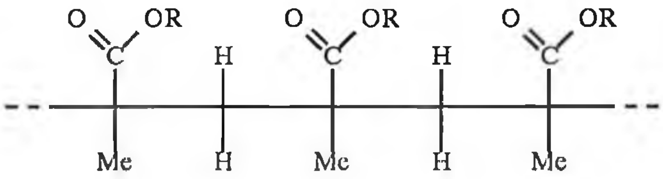


(b) m

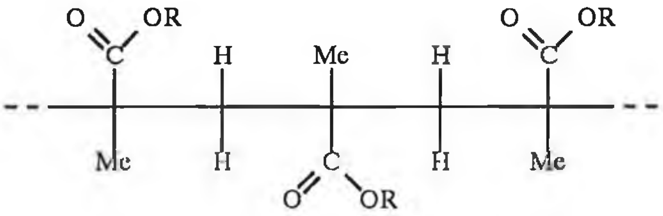
The syndiotactic or racemic dyad(a) has a two-fold axis of symmetry and consequently the two methylene protons are in equivalent environments on a time average over the chain conformation. These protons therefore have the same chemical shift and appear as a singlet despite strong two-bond or geminal coupling between them. The isotactic or meso (m) dyad (b) has a plane of symmetry but no two-fold axis and so the two protons are non-equivalent and have different chemical shifts. When there is no vicinal coupling to neighbouring protons, as is the case in PMMA, the syndiotactic sequences should exhibit a methylene singlet while the isotactic sequences should give two doublets, each with a spacing equal to the geminal coupling, ca. 15 Hz.[139]

The free radical polymerization product (atactic) and anionic polymerization product (isotactic) have been well studied using NMR[140]. The methylene spectrum of the anionic polymer is almost exclusively a pair of doublets (ca. 1.6 and 2.3ppm); The methylene spectrum of the free radical polymer is more complex, but the principal resonance (at ca. 1.9ppm) is a singlet, showing that this polymer is predominantly syndiotactic[139]. This is generally the case for vinyl polymers prepared with free radical initiators.[139]

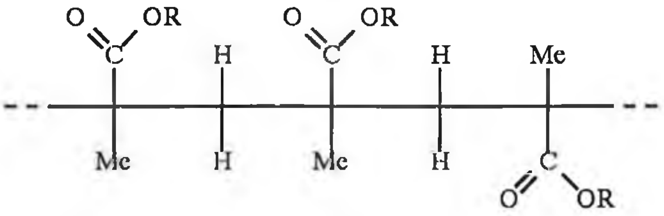
Somewhat more detailed, but not absolute, information can be gained from the methyl proton resonances near 1.2ppm. The C-methyl spectrum of anionic PMMA is a strong peak at 1.3ppm which correspond to the methyl in the centre monomer unit of isotactic triad sequence (a). (It may be more simply and appropriately designed by the m and r terminology, as indicated, mm). The C-methyl spectrum of the free radical polymer is more complex, three peaks (or, more correctly, groups of peaks) appearing in this spectrum. These correspond to the C-methyl groups in the centre monomer unit of the three possible triad sequences: isotactic (mm) (a), syndiotactic (rr) (b) and heterotactic (mr) (c). The ester methyl resonance at ca. 3.6ppm, which are less sensitive to stereochemistry.



(a) Isotactic, mm



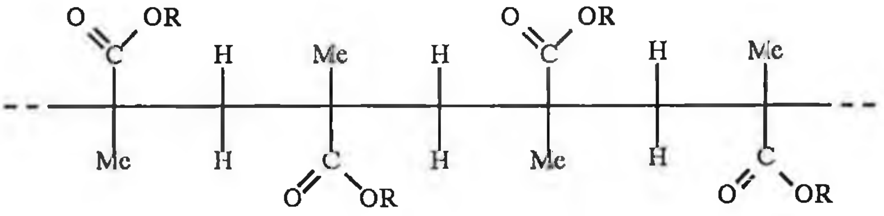
(b) Syndiotactic, rr



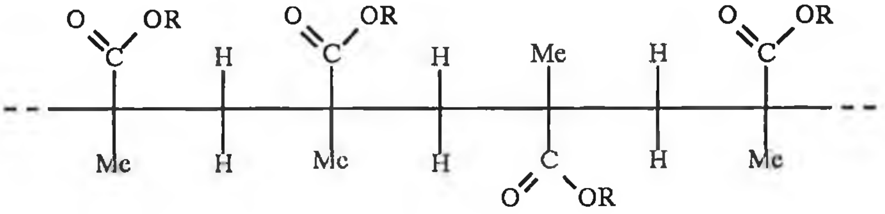
(c) Heterotactic, mr (or rm)

The assignment[139] of the ^{1}H-NMR spectrum of PMMA for the free radical polymerization product is : 1.05ppm (α - methyl (rr)), 1.16ppm (α - methyl (mr)), 1.32ppm (α - methyl (mm)).

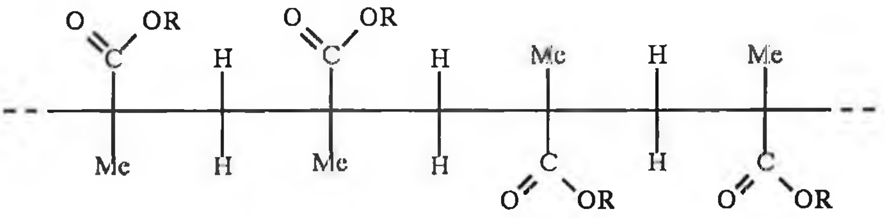
In the literature[139] the peaks for PMMA at 1.90ppm have been assigned to the β-methylene (rrr), at 2.0ppm to the β-methylene (mrr), and at 2.10ppm to the β-methylene (mrm). The chemical environment for the central β-methylene in sequence rrr, mrr and mrm are different.



(a) rrr



(b) mrr



(c) mrm

Comparison of the spectrum of poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130) in figure 3.6 with the PMMA spectra in the literatures[138, 139, 141], suggested the following possible assignments. The peak at 0.85ppm is for the rr α-methyl protons, the peak at 1.00ppm is for the mr α-methyl protons.The peak at 1.2ppm is mmrm α-methyl protons.the peak at 1.3ppm is mmmm α-methyl protons. The peak at 1.75ppm is rrr β-methylene protons, the one at 1.83ppm is mrr β-methylene, the one at 2.1ppm is mrm β-methylene. The low intensity of the mm triad sequences (mmrm at 1.2ppm and mmmm at 1.3ppm) suggested this polymer (130) is an atactic polymer.

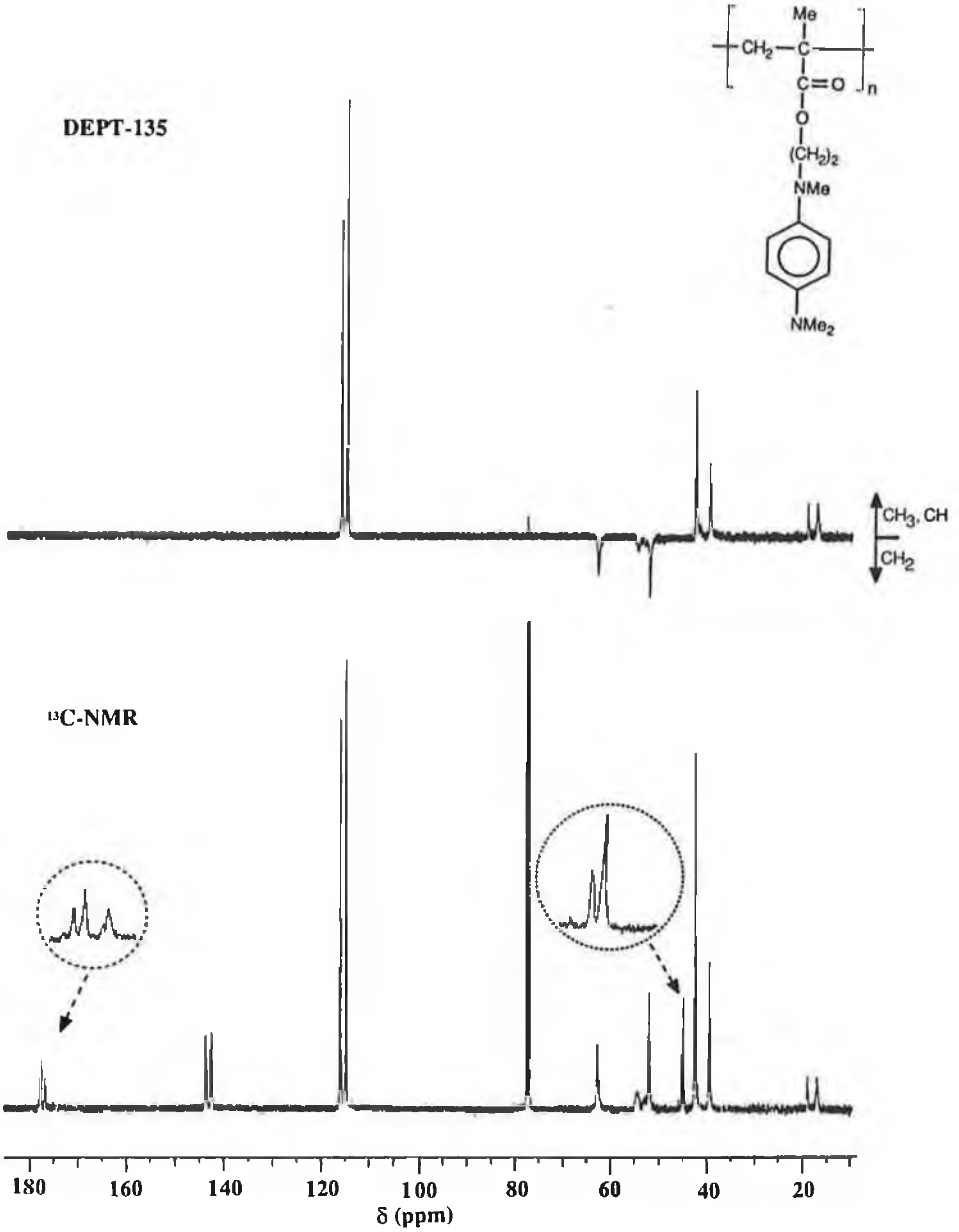


Figure 3.7 ^{13}C-NMR and DEPT-135 spectra of poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130) ($CDCl_3$, Bruker ACF-400)

The stereochemical microstructure was shown more clearly in the ^{13}C-NMR spectrum (fig. 3.7). The ^{13}C nucleus is of great potential interest for the study of polymer chains because it permits direct observation of the molecular skeleton, and because its range of chemical shifts is very large, encouraging the hope of seeing finer substructure than can be seen in proton spectra.

The ^{13}C-NMR spectra reported[141-144] for free radical polymerised PMMA have many similarities to the spectrum of poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130) (fig. 3.7). The assignment of the ^{13}C-NMR spectrum of this type of PMMA was carried out by comparison of the spectra of isotactic and syndiotactic PMMAs. Atactic PMMA, produced by radical polymerisation, was found to display two peaks for the α-methyl carbons. They were assigned to rr and mr (from high to low field) respectively. A similar but smaller separation was discernible in the quarternary carbon (i.e., α-carbon) resonances at ca. 45ppm. They were assigned to rr and mr respectively (from high to low field). More interesting is the carbonyl carbon region of the spectrum. Here there were three small peaks, assigned as mr, rr(rrrm), and rr(rrrr) (from high to low field) respectively.[144]

With the help of these assignment for PMMA, the assignment of the spectrum in figure 3.7 is greatly eased.. The assignment is tabulated in table 3.1 which is supported by DEPT-135 and C-H correlation spectrum.

In figure 3.7, the bottom spectrum is the normal ^{13}C-NMR spectrum, the upper spectrum being the DEPT-135 spectrum. In the DEPT-135 spectrum, methyl and methine peaks point up, the methylene peaks point down, quaternary carbons do not show up. So from this DEPT-135 spectrum, it is very easy to recognize the methyl carbons. There are four methyl peaks in the spectrum, the one at 42.20ppm may be assigned to the two identical N-methyls, the one at 39.28ppm to the other N-methyl, these were confirmed by a C-H correlation spectrum where both peaks were correlated with a peak at 2.80ppm in the ^{1}H-NMR spectrum which is characteristic of an p-dimethylamino-N-methylaniline unit. The intensity of the peak at 42.20ppm is approximately twice as high as that of the peak at 39.28ppm, so the former represents the two identical methyls.

Table 3.1 Assignment for the ^{13}C-NMR spectrum of poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130)

^{13}C-NMR (ppm)	DEPT-135	types of carbons	assignment
16.76	positive	primary	α - methyl protons (rr)
18.66	positive	primary	α - methyl protons (mr)
39.28	positive	primary	N-methyl
42.20	positive	primary	N-methyl
44.67	none	quaternary	α–C in polymer backbone (rr)
45.07	none	quaternary	α–C in polymer backbone (mr)
51.83	negative	secondary	CH_2-N
54.36	negative	secondary	β–CH_2 in polymer backbone
62.61	negative	secondary	CH_2-O
114.65	positive	tertiary	aromatic CH
115.72	positive	tertiary	aromatic CH
142.29	none	quaternary	aromatic C
149.43	none	quaternary	aromatic C
176.57	none	quaternary	carbonyl (mr)
177.36	none	quaternary	carbonyl (rr)
177.75	none	quaternary	carbonyl (rr)

From the polymer repeat unit only one methyl group remains unassigned so far. However ^{13}C-NMR spectrum clearly showed two methyls at 16.76 and 18.66ppm. These two peaks belong to the α–methyl groups, but different chemical environments exist for the methyls due to different stereochemical microstructures (rr and mr) in the polymer chain. So we can say that this polymer is a atactic polymer.

This steoreochemical effect can also be seen in the quaternary carbon in the polymer backbone, the carbonyl carbon and methylene in the polymer backbone. These are either in or connected directly to the polymer backbone, so their chemical environments are sensitive to the stereochemical microstructure of the polymer chain.

The two peaks at 44.67 and 45.08ppm in ^{13}C-NMR spectrum which do not show up in the DEPT-135 are assigned to the quaternary carbons in the polymer backbone. The presence of two peaks showed that there are two kinds of quaternary carbon in the polymer chain (rr, mr). The carbonyl region showed three peaks at 176.57, 177.36 and 177.75ppm, they are assigned to mr, rr, rr carbonyls. The methylenes in the polymer backbone showed up at 54.36ppm as a broad peak. Presumely the chemical shifts of the methylene in the different microstructures are close to each other, resulting in their overlapping to yield a broad peak.

In the ^{1}H-NMR spectrum (fig. 3.6) of poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130), there are tiny mm α-methyl peaks, while in the ^{13}C-NMR spectrum(fig. 3.7), the mm triad sequence was not observed. It may be due to the low abundance of ^{13}C nuclei. Both ^{1}H-NMR and ^{13}C-NMR spectra indicated that poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130) synthesized by free radical polymerisation is an atactic polymer.

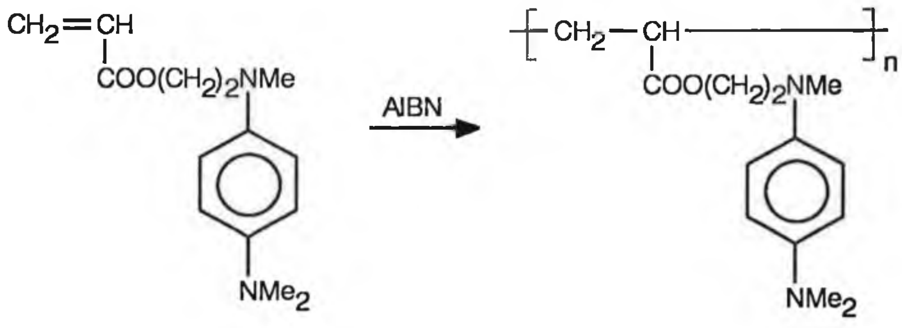
As mentioned in the introduction section of this chapter, in the propagation reaction the monomer can be attacked by a free radical on its head or on its tail resulting in three different chain structures (head-head, head-tail, tail-tail). However, Koenig[145] , based on many people's NMR work, concluded that polymers prepared by bond-opening polymerization of α-olefins, vinyl monomers and acrylic monomer have mainly head-to-tail linkages in the polymer chains. It seems highly probable that poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130) also has its repeat units arranged in the predominantly head-to-tail sequence.

For some cases the presence of head-to-head linkages formed by a radical polymerization has been assumed to occur by a termination reaction caused by radical recombination. Most of the monomers that have detectable amounts of head-to-head addition have a halogen substitutent, such as chlorine or fluorine, attached to the double bond. The amount of head-to-head structure can be varied in some cases, with higher polymerization temperature usually giving higher reverse monomer addition in the polymer chain. The relative orientation of the monomers during the polymerization is dependent on two factors:(i) the relative energy requirements of the transition states involved. (ii) the relative stabilities of the product radicals.

The initiation mode generating an active centre at the head of the monomer is favoured by both factors. That is, the steric requirements in the transition state are lessened, since the substitutent is one carbon removed from the attacking species. Additionally, the head has the substitutent in the position to stabilize the product by resonance or induction, while the tail has no effect of this kind. Consequently, the initiation step strongly favors the formation of the active site on the head of the repeating unit, and the propagating step proceeds predominantly by head-to-tail polymerization. For example, for styrene free radical polymerization leads to exclusively a head-to-tail structure.

It may be concluded therefore that for the polymers whose synthesis is reported in this chapter, chain isomerism through monomer enchainment can be ignored.

3.2.2 Synthesis and characterization of poly[2-(p-dimethylamino-N-methylanilino)ethyl acrylate] (131)



(101) (131)

Before polymerisation, the monomer 2-(p-dimethylamino-N-methylanilino)ethyl acrylate (101) was liberated from its toluene sulphonic acid salt (102) by treatment with aqueous sodium hydroxide, and extracted into diethyl ether. Removal of the solvent diethyl ether gave monomer (101). Because solution polymerization did not work well for (101), bulk polymerization was carried out. Its success may have been due to the avoidance of free radical transfer to solvent, and/or possibly to the much higher concentration of the monomer in a bulk polymerization due to the absence of the solvent. The conversion was lower than the polymerization of the first monomer (98). GPC measurement showed the number average molecular weight ($\overline{M}_n$) of this polymer (131) to be 23,400, corresponding to an average of approximately 94 monomer repeat units per polymer chain (131). The polydispersity index ($\overline{M}_w/\overline{M}_n$) = 1.91, indicated a narrow molecular weight distribution.

Like the polymer (130) in the previous section, infrared spectroscopy showed that the strong carbon-carbon double bond stretching peak which was present in the monomer's spectrum at 1631 cm^{-1} had disappeared from the polymer

(131) spectrum. ^{1}H-NMR and ^{13}C-NMR both showed the disappearance of the double bond and the presence of different stereomicrostrutures in the polymer.

A number of the peaks present in the ^{1}H-NMR spectrum may be readily assigned. Thus , the peak at 6.70ppm represents the four aromatic protons. The peak at 4.12ppm is that of the OCH_2 group and that at 3.38ppm arises from the NCH_2 group. The peak at 2.79ppm represents the three methyls in the structure. The peaks in the range from 1.1ppm to 2.6ppm are particularly interesting, arising from the methine and methylene protons in the polymer backbone. Integration from 2.1 to 2.6ppm indicated one proton in this range, with one broad peak at 2.34ppm and a small shoulder at 2.18ppm. They arise from the methine groups in the polymer backbone. Integration over the range 1.1 - 2.1ppm revealed two protons, giving rise to three broadened medium-sized peaks and one small one. All are assigned to the methylene protons in the polymer backbone. .The presence of a number of different methylene environments is consistent with the presence of a number of different stereostructures present in the polymer, and that it is also atactic. Precise assignment of the peaks is difficult. The closest model NMR spectrum is that of poly(methyl acrylate)(PMA). Detailed assignment of its spectrum is complicated by the presence of vincinal coupling.[146] It has however been assigned, though detailed spin models[136, 147] were required to solve the problem. Based on the PMA assignment[134, 147, 148] the backbone methine and methylene protons of polymer (131) may be tentatively assigned as follows. The peak at 1.62ppm is that from the racemic methylene protons, those at 1.42 and 1.87ppm are assigned to the meso-methylene protons,and that at 2.34ppm to the methine protons.

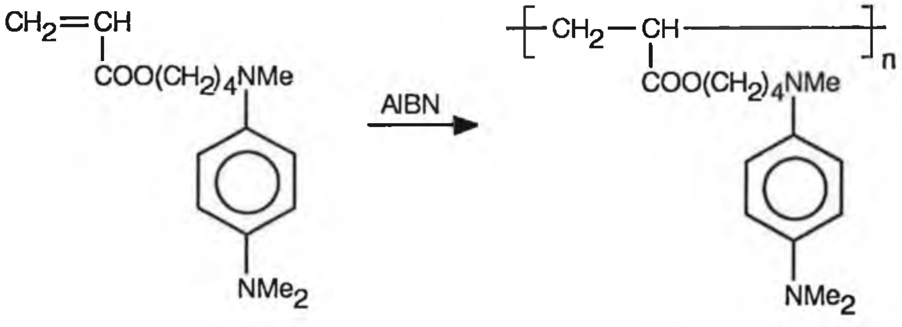
The assignments of the ^{13}C-NMR spectrum of polymer (131) with the support of a DEPT-135 spectrum are listed in table 3.2

Table 3.2 Assignment of ^{13}C-NMR spectrum of poly[2-(p-dimethylamino-N-methylanilino)ethyl acrylate] (131)

^{13}C-NMR (ppm)	DEPT-135	types of carbons	assignment
35.21	negative	CH_2	CH_2 in the polymer backbone (broad)
39.34	positive	CH_3	NMe
41.43	positive	CH	CH in the polymer backbone
42.52	positive	CH_3	NMe_2
51.95	negative	CH_2	NCH_2
61.85	negative	CH_2	OCH_2
114.40	positive	CH	aromatic CH
116.10	positive	CH	aromatic CH
142.70	none	C	aromatic C
143.85	none	C	aromatic C
174.13	none	C	carbonyl

The ^{13}C-NMR spectra of both isotactic(anionic polymerization) and atactic PMA(free radical polymerization) were reported.[147] The atactic PMA has a broad methylene (or a group of peaks) peak, while the isotactic one a relative sharp one. The ^{13}C-NMR spectrum of poly[2-(p-dimethylamino-N-methylanilino)ethyl acrylate] (131) is similar to that of the atactic PMA, indicating this polymer (131) polymerised by free radical initiation is atactic.

3.2.3 Synthesis and characterization of poly[4-(p-dimethylamino-N-methylanilino)butyl acrylate] (132)



(104) (132)

Before polymerisation, the monomer 4-(p-dimethylamino-N-methylanilino)butyl acrylate (104) was liberated from its 3,5-dinitrobenzoic acid salt (105) by treatment with aqueous sodium hydroxide, and extracted into diethyl ether. Removal of the solvent diethyl ether gave monomer (104). This monomer did not undergo solution polymerization and so was polymerized in bulk with AIBN as initiator. Conversion was low (22%). GPC measurement showed the number average molecular weight ($\overline{M}_n$) of this polymer to be 33,700, corresponding to an average of approximately 122 monomer repeat units per polymer chain. The polydispersity index ($\overline{M}_w/\overline{M}_n$) = 2.34, indicated a narrow molecular weight distribution.

The IR spectrum of the product (132) showed the absence of a carbon-carbon double bond stretch at 1631 cm^{-1}, present in the monomer (104), as expected for the required polymer (132). The ^{1}H-NMR spectrum of the product was also consistent with polymerization having occurred. There were no vinyl protons present, instead three additional proton absorption appeared in the aliphatic range.The ^{13}C-NMR spectrum of the product (132), showed the absence of the two vinyl carbons at 128.12 and 130.92ppm, present in the monomer salt

(105), instead two additional carbons appeared at 35.00 and 41.34ppm in the ^{13}C-NMR spectrum of the product, as expected for the required polymer (132).

Table 3.3 Assignment of ^{1}H-NMR spectrum of poly[4-(p-dimethylamino-N-methylanilino)butyl acrylate] (132)

^{1}H-NMR (ppm)	assignment
1.30	CH_2 in polymer backbone(m)
1.62	CH_2 in polymer backbone(r), and two CH_2s between CH_2N and CH_2O
1.96	CH_2 in polymer backbone(m)
2.31	CH in polymer backbone
2.86	three NMe
3.18	CH_2N
4.02	CH_2O
6.72	aromatic CH

The assignment of the ^{1}H-NMR spectrum of this polymer (132) is tabulated in table 3.3. The assignment for the peaks from 2.5 - 7.0ppm is clear and straightforward as indicated in table 3.3. However the region from 1.1 to 2.5 is complicated. The peak at 2.31ppm represents a methine group in the polymer backbone with an integration of one proton. Integration for the range 1.1 - 2.1ppm shows six protons, with one major peak at 1.62ppm, and two smaller peaks at 1.30 and 1.96ppm. In the COSY spectrum of this polymer, the peak at 1.62ppm is shown to be coupled with the N-methylene at 3.18ppm, the O-methylene at 4.02ppm and with the CH in the polymer backbone at 2.31ppm, indicating that the resonances for methylene connected to the N-methylene, the methylene connected to the O-methylene, and the methylene in the polymer backbone all coincide at 1.62ppm. The peaks at 1.30 and 1.96ppm are also assigned to methylene protons in the polymer backbone, indicating the presence of different stereostructures. Based on the PMA assignment.[134], [147, 148] the methylene at 1.62ppm is assigned to racemic, and the ones at 1.30 and 1.96ppm to the meso-methylene protons.

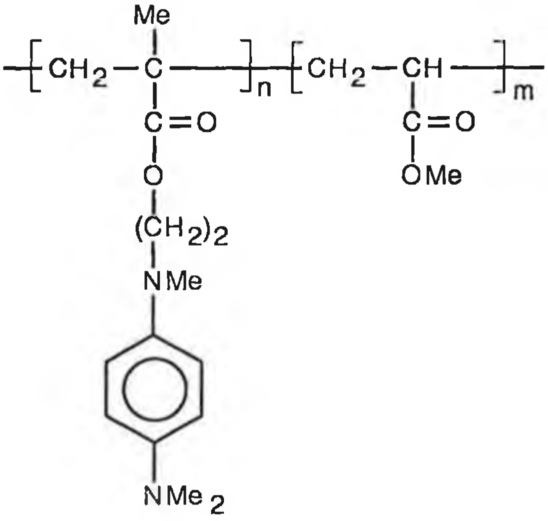
The assignment of the ^{13}C-NMR spectrum of polymer (132) is tabulated in table 3.4, The broad peak at 35.00ppm for the methylene groups in the polymer backbone is similar to that of atactic PMA[139, 149], suggesting this polymer is atactic. The assignments are supported by the DEPT-135 spectrum.

Table 3.4 Assignment of ^{13}C-NMR spectrum of poly[4-(p-dimethylamino-N-methylanilino)butyl acrylate] (132)

^{13}C-NMR (ppm)	DEPT-135	types of carbons	assignment
23.07	negative	CH_2	CH_2 connected with CH_2N
26.24	negative	CH_2	CH_2 connected with CH_2O
35.00 (broad)	negative	CH_2	CH_2 in polymer backbone
39.65	positive	CH_3	NMe
41.34	positive	CH	CH in polymer backbone
42.41	positive	CH_3	NMe_2
53.95	negative	CH_2	CH_2-N
64.46	negative	CH_2	CH_2-O
115.44	positive	CH	aromatic CH
115.98	positive	CH	aromatic CH
142.26	none	C	aromatic C
142.89	none	C	aromatic C
174.25	none	C	carbonyl

3.2.4 Synthesis and characterization of copolymers of 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98) with methyl acrylate

There are two purposes for to making the copolymers. One is to separate the electroactive centres thereby removing each redox centre from the possibility of interacting with its neighbours. Another purpose is to reduce solubility. Homopolymer (130) is soluble in acetonitrile and propylene carbonate, common solvent for electrolyte systems. However polystyrene is insoluble in these solvents. A copolymer of monomer (98) with styrene therefore is likely to be also insoluble in acetonitrile and propylene carbonate.



10% (133); 5% (134)

Copolymerization of monomer (98) with methyl acrylate was carried out by a free radical process using AIBN as initiator. The compositions were controlled by the starting ratios of the two monomers in the reaction mixture.

The compositions of the copolymers reported in this thesis is defined as the percentage of electroactive monomer units present in the polymer chain.

Two copolymers, (133) and (134), with different compositions were synthesized. Table 3.5 shows the two copolymers, their compositions are approximately 10% and 5% respectively. Calculation of the compositions of the copolymers by microanalysis and by ^{1}H-NMR compare well with the monomers ratios in the reaction mixtures.

Table 3.5 Compositions of the copolymer calculated using three ways

copolymers	composition from monomer ratio	composition from microanalysis	composition from ^{1}H-NMR
133	11.%	11%	11%
134	5%	5%	5%

Because the whole range of compositions of this copolymer were not synthesized, it is too early to comment on the reactivity ratios[121] of the two monomers in this copolymerization. However, at least at low composition range (< 10%), the compositions of the copolymers are very close to the composition of monomers added at the beginning.

GPC measurement showed the number average molecular weights ($\overline{M}_n$) of the copolymers to be 55,300 for the 10% copolymer (133), and 29,600 for the 5% copolymer (134). The polydispersity index was $\overline{M}_w/\overline{M}_n = 2.05$ for the 10% one (133) and $\overline{M}_w/\overline{M}_n = 3.55$ for the 5% one (134).

In the infrared spectrum (fig. 3.8) of the copolymer, the carbon-carbon double bond stretch peak at 1630 cm^{-1} which is present in the IR spectra of both monomers is absent and provides evidence for polymerization having occurred. In addition there is a peak present at 1518cm^{-1} which is absent from the IR spectrum of the homopolymer of methyl acrylate. This provides evidence for incorporation of (98) in the copolymer since the spectrum of homopolymer poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130) also displays a very strong peak at 1518 cm^{-1} due to aromatic ring vibrations.

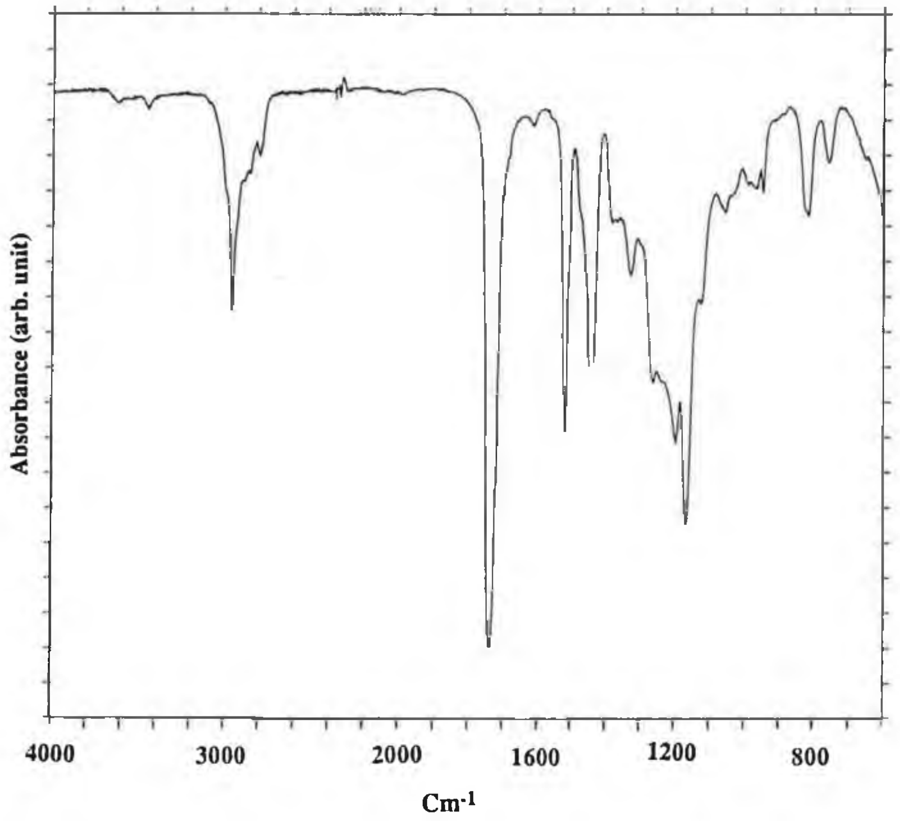


Figure 3.8 IR spectrum for the copolymer (10%) (133) of 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98) with methyl acrylate

^{1}H-NMR and ^{13}C-NMR spectra both showed the disappearance of the vinyl groups from both monomers in the products, indicating the polymerisation having occurred.

The complete assignment of the ^{1}H-NMR spectrum for the range 0.8 - 2.6ppm is difficult, because it is complicated by different stereochemical microstructures and different monomer units, and there are serious overlapping of peaks in this range. However the other peaks can be assigned clearly. The N-methyl substituents gave rise to two peaks at 2.84 (NMe$_2$) and 2.90 (NMe)ppm, the N-methylene appeared at 3.50ppm, the OMe appeared at 3.57 (mr) and 3.62 (rr) ppm, the O-methylene protons appeared at 4.12ppm, and the aromatic protons appeared at 6.78ppm. The two OMe peaks and the complication in the range

0.6 - 2.6ppm indicate different stereochemical microstructures present in the copolymers.

The ^{13}C-NMR spectra of copolymer (133) is easier to assign because of good resolution. With the help of DEPT-135 and comparison with the spectrum of homopolymer (130) in figure 3.7, the assignment of this spectrum (fig. 3.4) is listed in table 3.6. The C-H correlation spectrum assisted in the assignment, being especially useful in identifying the origins of the peak at 42.10ppm (correlated with the methyl at 2.84ppm in the ^1H-NMR spectrum), and of those at 41.21 and 41.07ppm (both correlated with the methine at 2.30ppm in the ^1H-NMR spectrum).

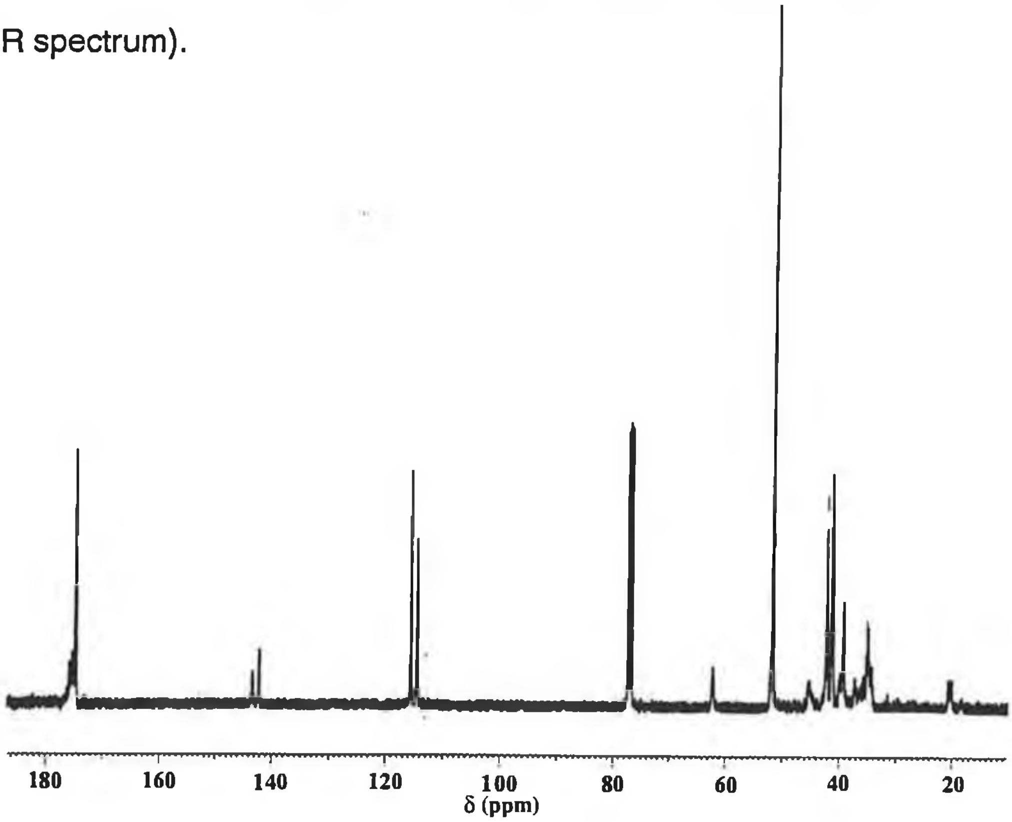


Figure 3.9 ^{13}C-NMR spectrum for the copolymer of 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate with methyl acrylate (composition, 10%) (133)

Table 3.6 Assignment of the ^{13}C-NMR spectrum for the copolymer (133) of 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate with methyl acrylate

^{13}C-NMR (ppm)	DEPT-135	carbons	from unit A*	from unit B*
19.92	positive	CH_3	-Me	
20.43	positive	CH_3	-Me	
34.18	negative	CH_2		backbone
34.86	negative	CH_2		backbone
35.06	negative	CH_2		backbone
35.42	negative	CH_2		backbone
37.13	negative	CH_2	backbone	
39.15	positive	CH_3	NMe	
41.07	positive	CH		backbone
41.21	positive	CH		backbone
42.10	positive	CH_3	$-NMe_2$	
45.14	none	C	backbone	
51.60	positive	CH_3		-OMe
51.68	negative	CH_2	$-CH_2N$	
62.16	negative	CH_2	$-CH_2O$	
114.58	positive	CH	aromatic	
115.69	positive	CH	aromatic	
142.30	none	C	aromatic	
143.50	none	C	aromatic	
174.78	none	C		carbonyl
175.28	none	C	carbonyl	
175.59	none	C	carbonyl	
175.80	none	C	carbonyl	

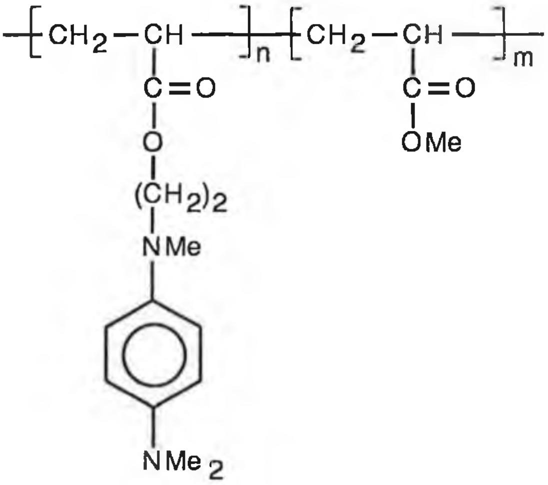
*Unit A: repeat unit derived from 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate

Unit B: repeat unit derived from methyl acrylate

Like the homopolymer of poly(2-(p-dimethylamino-N-methylanilino)ethyl methacrylate) (130) (fig. 3.7), different stereostructures showed up in this copolymer (133) as well. The most obvious peaks are the methyl peak at 19.92

and 20.43ppm, similar to those of its homopolymer (130). Also in the carbonyl range, one peak at 174.78ppm is from the methyl acrylate units, the other three being similar to those of the homopolymer (130). The methylenes from the methyl acrylate units in the copolymer backbone appeared as a few overlapped peaks from 34.00 to 36.00ppm. The two peaks at 41.07 and 41.21ppm arise from the stereochemical environments within the methyl acrylate units, and are similar to those of an atactic PMA.[149]

3.2.5 Synthesis and characterization of copolymers of 2-(p-dimethylamino-N-methylanilino)ethyl acrylate (101) with methyl acrylate



(135) 10%; (136) 5%

The copolymerisations of 2-(p-dimethylamino-N-methylanilino)ethyl acrylate (101) with methyl acrylate was carried out successfully with benzene as solvent. Benzene is a good solvent for solution free radical polymerization, the transfer constant of free radicals to benzene is very low. GPC measurements show the copolymerisation products (135) and (136) are high molecular weight substances with narrow molecular weight distributions. In the IR spectra of copolymers (135) and (136), there is a peak at 1518 cm^{-1} (aromatic vibration) which is absent from the IR spectrum of PMA, indicating the incorporation of the electroactive monomer in the copolymer. In the IR spectrum of homopolymer poly[2-(p-dimethylamino-N-methylanilino)ethyl acrylate] (131), the peak at 1518 cm^{-1} is very strong.

The ^{1}H-NMR (fig. 3.10) and ^{13}C-NMR (fig. 3.11) spectra are consistent with copolymerisation having occurred.

For example, the ^{1}H-NMR spectrum (fig. 3.10) for 10% copolymer (135) shows clearly the carbonmethoxy group (3.70ppm) from the methyl acrylate monomer units, in addition to aromatic (6.70ppm), O-methylene (4.20ppm), N-methylene (3.45ppm) and N-methyls (2.85ppm) protons from the 2-(p-dimethylamino-N-methylanilino)ethyl acrylate (101) units. The different peaks between 1.2 and 2.0ppm confirm the presence of different stereochemical environments for the methylenes in copolymer (135). The peak at 2.30ppm is assigned to the methine groups in the polymer backbone.

The ^{13}C-NMR spectrum (fig. 3.11) gave more detailed informations about the structure of copolymer (135).The assignment of the ^{13}C-NMR is tabulated in table 3.7.This assignment is supported by the DEPT-135 and C-H correlation spectra.

Figure 3.10 ^{1}H-NMR spectrum of the copolymer 2-(p-dimethylamino-N-methylanilino)ethyl acrylate (101) with methyl acrylate

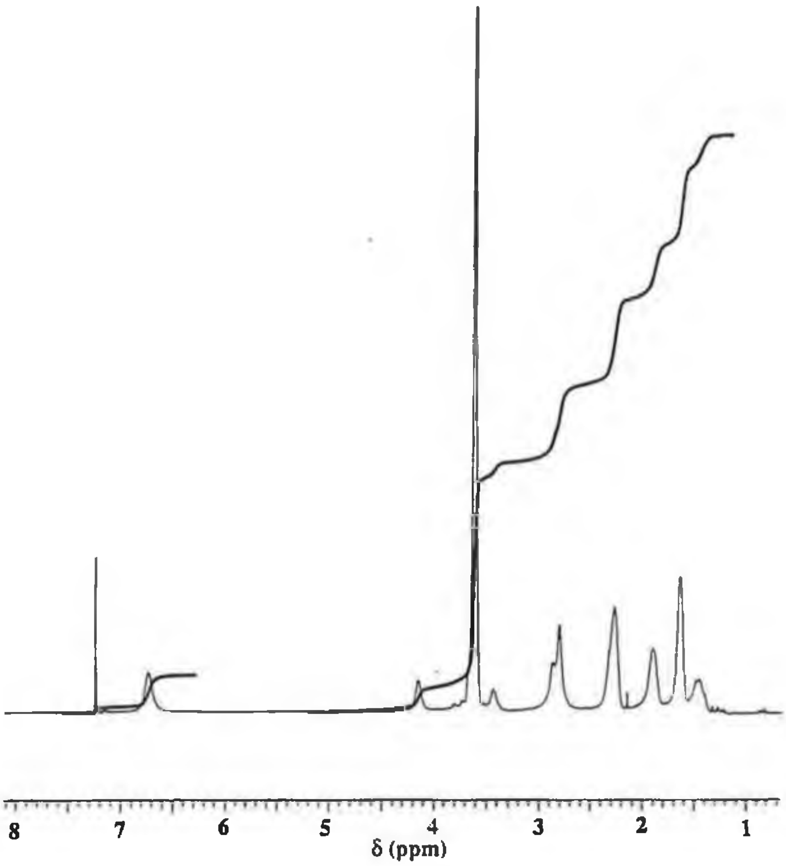


Figure 3.10 ^{1}H-NMR spectrum of the copolymer 2-(p-dimethylamino-N-methylanilino)ethyl acrylate (101) with methyl acrylate

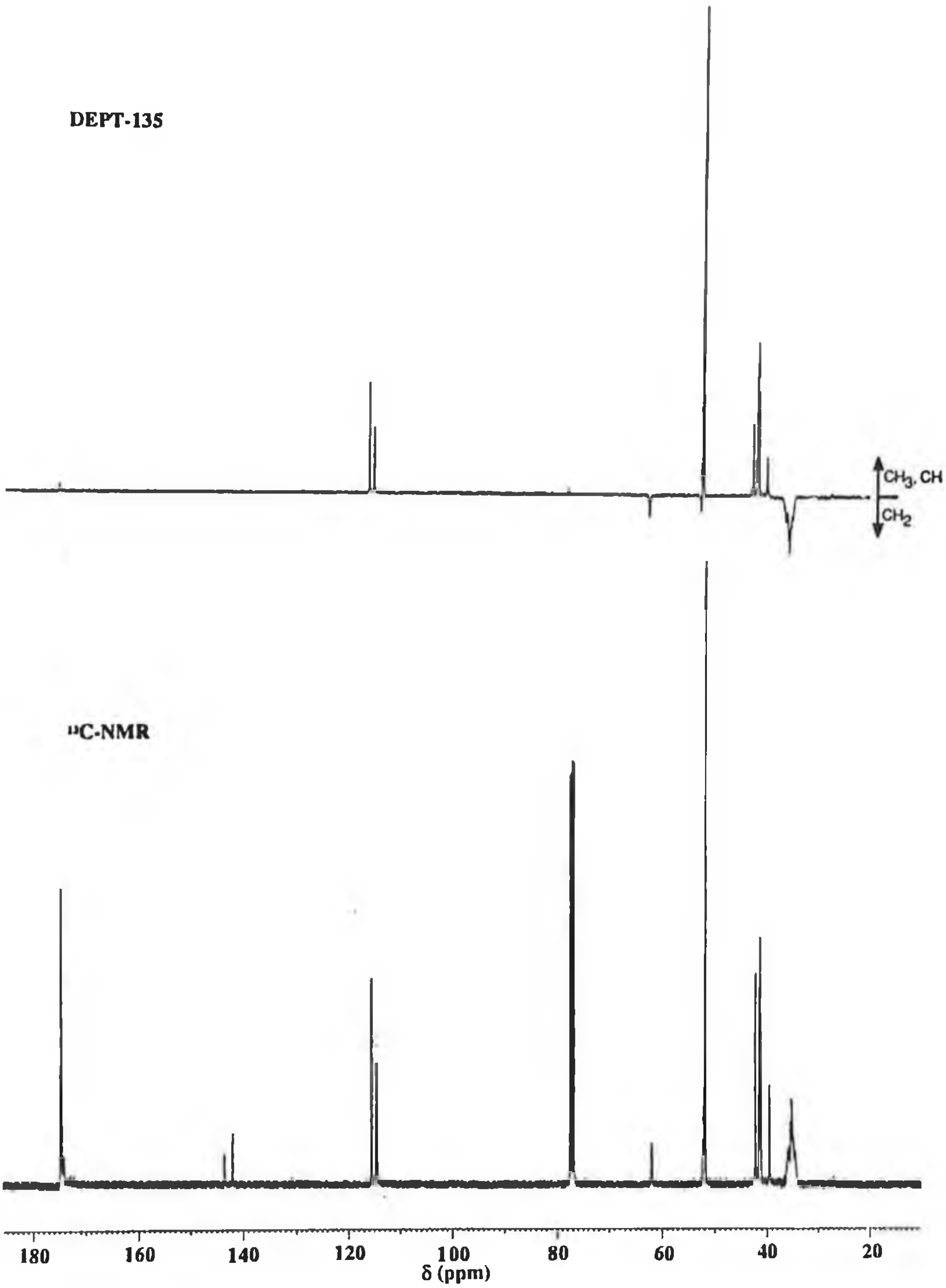


Figure 3.11 ^{13}C-NMR and DEPT-135 spectra for the copolymer (135) of 2-(p-dimethylamino-N-methylanilino)ethyl acrylate (101) with methyl acrylate (composition 10%)

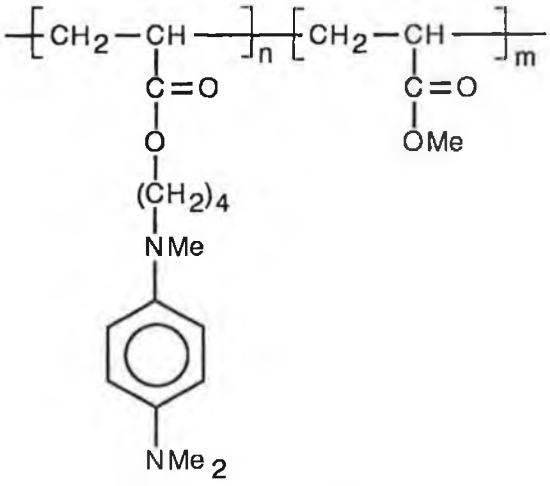
Table 3.7 Assignment of the ^{13}C-NMR spectrum for the copolymer (135) of 2-(p-dimethylamino-N-methylanilino)ethyl acrylate (101) with methyl acrylate

^{13}C-NMR (ppm)	DEPT-135	carbons	unit A*	unit B*
34.87	negative	CH_2		backbone
35.08	negative	CH_2		backbone
35.46	negative	CH_2		backbone
39.33	positive	CH_3	-NMe	
41.05	positive	CH		backbone
41.21	positive	CH		backbone
42.06	positive	CH_3	$-NMe_2$	
51.71	positive	CH_3		CH_3O-
52.08	negative	CH_2	$-CH_2N-$	
61.86	negative	CH_2	$-CH_2O-$	
114.62	positive	CH	aromatic	
115.59	positive	CH	aromatic	
142.05	none	C	aromatic	
143.67	none	C	aromatic	
174.33	none	C	carbonyl	
174.83	none	C		carbonyl

*Unit A: repeat unit derived from 2-(p-dimethylamino-N-methylanilino)ethyl acrylate
Unit B: repeat unit derived from methyl acrylate

The tertiary carbon peak from unit A, is probably hidden under the peak at 39.33ppm. Also the CH_2s from unit A is probably hidden under the broad peaks from 34 - 36ppm.

3.2.6 Synthesis and characterization of copolymers of 4-(p-dimethylamino-N-methylanilino)butyl acrylate (104) with methyl acrylate



(137) 15% ; (138) 5%

Two copolymer compositions, (137) and (138), for 4-(p-dimethylamino-N-methylanilino)butyl acrylate (104) with methyl acrylate were synthesized, GPC measurement shows that their molecular weight are quite high and molecular weight distributions are narrow. For polymer (137) $\bar{M}_n$ = 81,300, $\bar{M}_w/\bar{M}_n$ = 1.47, for polymer (138), $\bar{M}_n$ = 37,700, $\bar{M}_w/\bar{M}_n$ = 1.85.

The IR spectra of copolymers (137) and (138) of show the characteristic aromatic absorbtion band at 1518 cm^{-1}, confirming the incorporation of the electroactive monomer (104) in the copolymer. Both ^{1}H-NMR and ^{13}C-NMR spectra are also consistent with the copolymerisation having occurred.

The COSY spectrum for copolymer (137) gave useful information about its structure (fig. 3.12). The presence of a carbonmethoxy group (3.60ppm) and aromatic (6.65ppm), O-methylene (3.95ppm), N-methylene (3.12ppm), and N-methyl (2.75ppm) units confirmed the presence of both monomers in the copolymer .

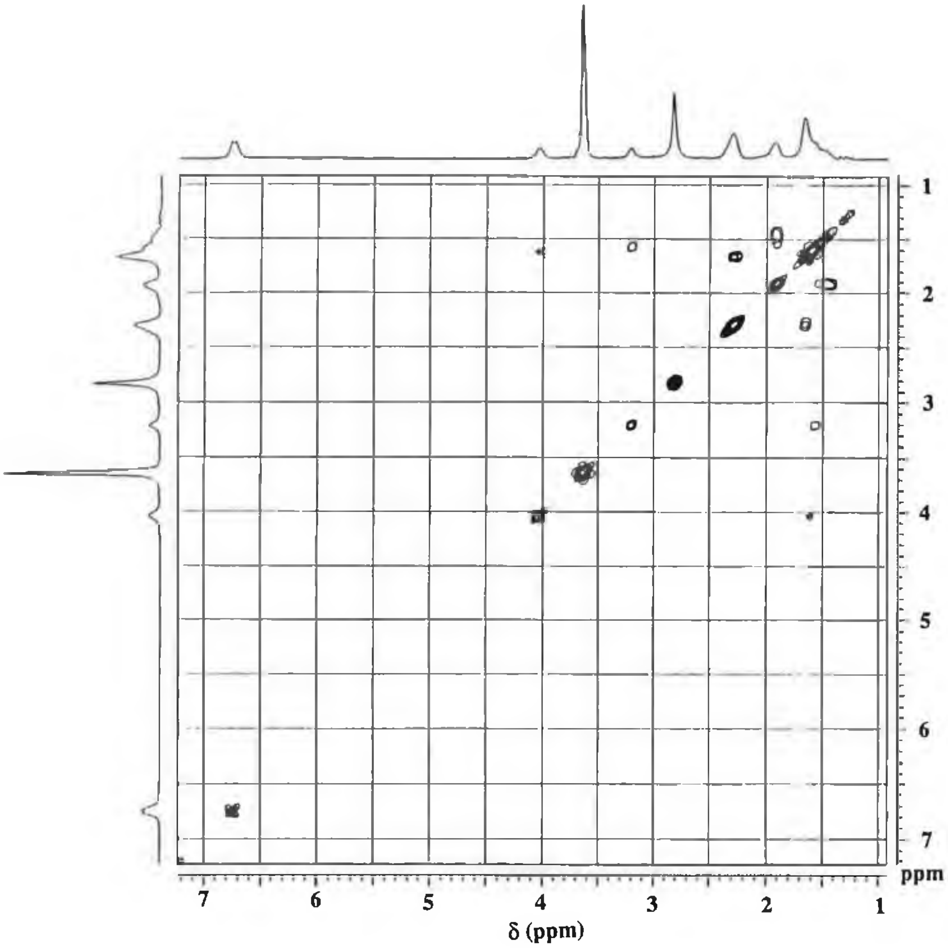


Figure 3.12 COSY spectrum for the copolymer (137) of 4-(p-dimethylamino-N-methylanilino)butyl acrylate (104) with methyl acrylate (composition 15%)

From the couplings listed in table 3.8, it can be seen that the two side-chain methylenes linking the O-methylene and N-methylene groups both appeared in the overlapped peak at 1.4 - 1.7ppm. Methylenes from the polymer backbone also contribute to absorption in this region. Detailed assignment of the range 1.0 - 2.6ppm is difficult due to overlapping.

Table 3.8 Couplings observed in the COSY spectrum in figure 3.12

COSY peaks coupling	with peaks
1.90ppm	1.4 - 1.7ppm
2.35ppm	1.4 - 1.7ppm
3.12ppm	1.4 - 1.7ppm
3.95ppm	1.4 - 1.7ppm

The ^{13}C-NMR and DEPT-135 spectra (fig.3.13) showed clearly the structure of copolymer (137). The C-H correlation spectrum assisted in the assignment of some additional peaks. Table 3.9 lists some of the useful couplings observed in the C-H correlation spectrum.

Table 3.9 C-H correlation coupling

^{1}H-NMR	assignment	^{13}C-NMR
3.95ppm	$-OCH_2-$	64.47ppm
3.60ppm	$-OCH_3$	51.59ppm
2.35ppm	CH in backbone	41.28 & 41.06ppm

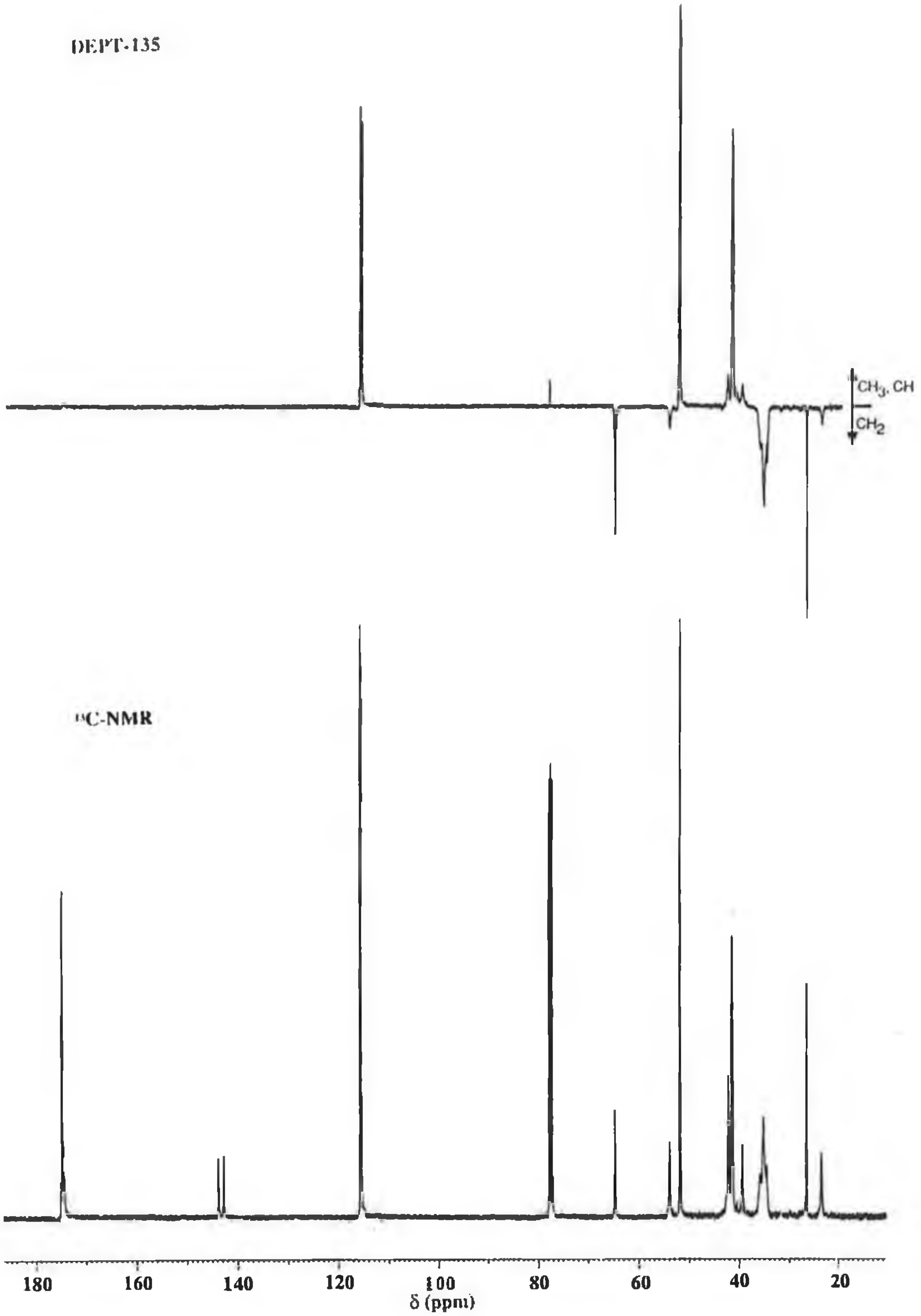


Figure 3.13 ^{13}C-NMR and DEPT-135 spectra for the copolymer (137) of 4-(p-dimethylamino-N-methylanilino)butyl acrylate (104) with methyl acrylate (composition 15%).

Table 3.10 Assignment of the ^{13}C-NMR spectrum for the copolymer of 4-(p-dimethylamino-N-methylanilino)butyl acrylate (104) with methyl acrylate

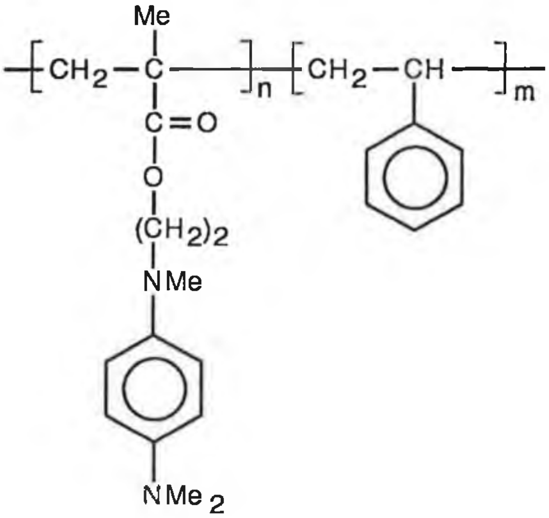
^{13}C-NMR (ppm)	DEPT-135	carbons	unit A*	unit B*
23.18	negative	CH_2	$-CH_2-C-N$	
26.25	negative	CH_2	$-CH_2-C-O$	
34.21	negative	CH_2		backbone
34.84	negative	CH_2		backbone
35.56	negative	CH_2		backbone
39.15	positive	CH_3	-NMe	
40.20	positive	CH	backbone	
41.06	positive	CH		backbone
41.28	positive	CH		backbone
41.96	positive	CH_3	$-NMe_2$	
51.59	positive	CH_3		CH_3O-
53.68	negative	CH_2	$-CH_2N-$	
64.47	negative	CH_2	$-CH_2O-$	
115.21	positive	CH	aromatic	
115.43	positive	CH	aromatic	
142.59	none	C	aromatic	
143.60	none	C	aromatic	
174.40	none	C	carbonyl	
174.74	none	C		carbonyl

*Unit A: repeat unit derived from 4-(p-dimethylamino-N-methylanilino)butyl acrylate

Unit B: repeat unit derived from methyl acrylate

The methylenes in the polymer backbone from unit A may be hidden under the broad peaks around 34.84ppm.

3.2.7 Synthesis and characterization of copolymers of 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98) with styrene



20% (139); 5% (140)

In this chapter, copolymers of the three different electroactive monomers (98), (101) and (104) with styrene were synthesized. Polystyrene is insoluble in acetonitrile and propylene carbonate. whereas the electroactive homopolymers (130) (131) (132) are soluble in these solvents. In order to achieve insoluble copolymers for investigation with acetonitrile or propylene carbonate, only low composition copolymers were synthesized. For each electroactive monomer, two copolymer compositions were used, and the contents of these electroactive units in the copolymers were less than 20%.

This section is concerned with the copolymers of 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate with styrene. Two compositions were synthesized (135 and 136). The higher composition one (139) is used to discuss their structures.

GPC measurement shows polymer (139) to be a high molecular weight substance with number-average molecular weight ($\overline{M}_n$) 47,500, and polydispersity index ($\overline{M}_w/\overline{M}_n$) 1.73, indicating a narrow molecular weight distribution. The composition of the copolymer is approximately 20% as calculated by elemental microanalysis. The infrared spectrum shows clearly that the electroactive monomer has been incorporated in the polymer (139), since it displays a significant C=O stretch peak at 1724 cm^{-1}.

The ^{1}H-NMR spectrum is also consistent with copolymerisation having occurred. There are no vinyl protons present. It also shows clearly that the electroactive monomer (98) has been incorporated in the polymer (139), since it displayed N-methyl protons at 2.82ppm.

Detailed assignment of the ^{1}H-NMR spectrum of copolymer (139) was difficult because of the complexities arising from proton coupling and the overlapping of the resonances resulting from the large number of different stereochemical microstructures, each with slightly differing chemical shifts. There have not been many investigations of the stereochemical microstructure of polystyrene using ^{1}H-NMR, due to the difficulties in assignment.[139, 140, 150]

The ^{13}C-NMR spectrum gives more detailed information about the structure of copolymer(139) (fig. 3.14).

The CH_2s in the polymer backbone from the electroactive monomer units probably are hidden under the CH_2s from the styrene units. The ^{13}C-NMR spectrum of homopolymer poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130) (fig. 3.7) and that of polystyrene assisted in the assignment of the spectrum (fig. 3.14) for copolymer (135), indicating that both electroactive monomer (98) and styrene had been incorporated.

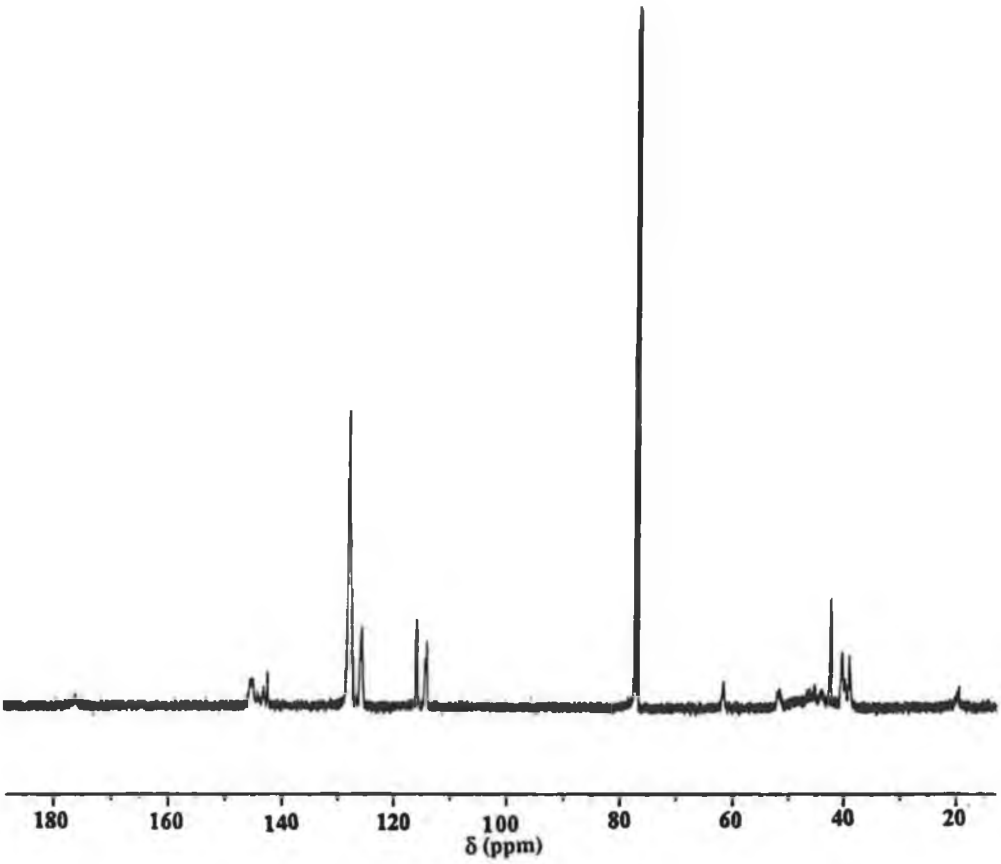


Figure 3.14 ^{13}C-NMR spectrum of the copolymer (139) 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98) with styrene (composition, 20%)

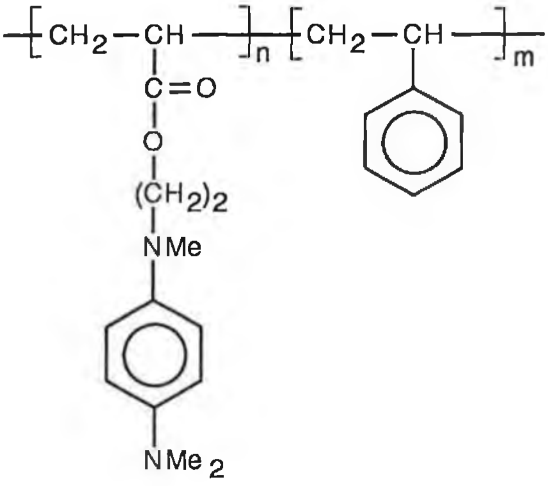
Table 3.11 Assignment of the ^{13}C-NMR spectrum of the copolymer 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98) with styrene

^{13}C-NMR (ppm)	DEPT-135	carbons	from unit A*	from unit B*
19.50	positive	CH_3	Me-backbone	
39.12	positive	CH_3	NMe	
39.87	positive	CH		backbone
40.39	positive	CH		backbone
42.40	positive	CH_3	NMe_2	
43.90	none	C	backbone	
45.33	negative	CH_2		backbone
46.17	negative	CH_2		backbone
46.75	negative	CH_2		backbone
51.66	negative	CH_2	$-CH_2N-$	
61.75	negative	CH_2	$-CH_2O-$	
114.13	positive	CH	aromatic	
115.90	positive	CH	aromatic	
125.70	positive	CH		aromatic
127.99	positive	CH		aromatic
142.53	none	C	aromatic	
143.17	none	C	aromatic	
145.19	none	C		aromatic
176.22	none	C	carbonyl	

*Unit A: repeat unit derived from 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate

Unit B: repeat derived from styrene.

3.2.8 Synthesis and characterization of copolymers of 2-(p-dimethylamino-N-methylanilino)ethyl acrylate (101) with styrene


(141) 15%; (142) 5%

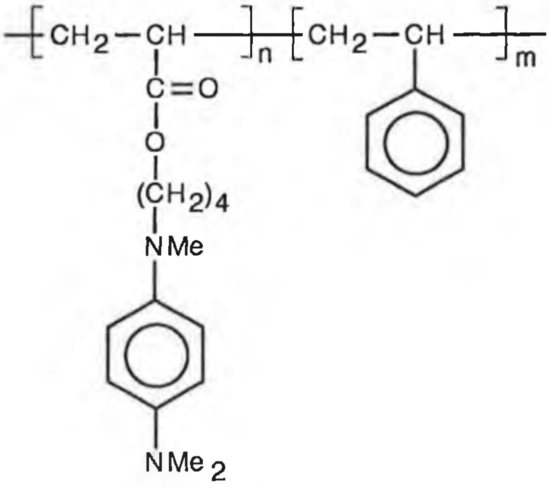
Copolymerisations of 2-(p-dimethylamino-N-methylanilino)ethyl acrylate (101) with styrene gave high molecular weight substances. The 15% copolymer (141) had a number-average molecular weight ($\overline{M}_n$) of 51,650, and a polydispersity index ($\overline{M}_w/\overline{M}_n$) of 1.75.

Infrared spectra show a medium sized carbon-oxygene double bond stretch at 1729cm^{-1}in the copolymers (141) and (142) which is not present in the spectrum of polystyrene indicating the incorporation of the electroactive unit (101).

Both the ^{1}H-NMR and ^{13}C-NMR spectra are also consistent with the copolymerisation having occurred. The ^{13}C-NMR spectrum especially gave more detailed information about the structure of the copolymer. The aromatic methine carbons from the styrene units appeared at 125.71, 127.89 and 128.07ppm. The aromatic quaternary carbon from styrene unit appeared at 145.14ppm. The peaks at 175.72 (carbonyl), 143.62 (aromatic C), 142.12

(aromatic C), 115.93 (aromatic CH), 114.39 (aromatic CH), 61.50 (OCH_2), 52.00 (NCH_2)ppm are from the electroactive monomer units, their assignments being similar to those for homopolymer of poly[2-(p-dimethylamino-N-methylanilino)ethyl acrylate] (131) (table 3.2). In the ^{13}C-NMR spectrum of copolymer (141), there are serious overlappings between 37 and 48ppm. All the methylene and methine carbons in the polymer backbone from both monomer units and from the N-methyl carbons appeared in this range. Detailed assignment of this region is difficult, even DEPT-135 spectrum did not help much due to the overlapping.

3.2.9 Synthesis and characterization of copolymers of 4-(p-dimethylamino-N-methylanilino)butyl acrylate (104) with styrene



(143) 15%; (144) 5%

Like the other two electroactive monomers (98) and (101), monomer (104) readily copolymerized with styrene . Two copolymer compositions (143) and (144) were synthesized. Both of them have high molecular weights and narrow molecular weight distributions. For copolymer (143) $\overline{M}_n$ = 42,250, $\overline{M}_w/\overline{M}_n$ = 1.83, for polymer (144), $\overline{M}_n$ = 52,600, $\overline{M}_w/\overline{M}_n$ = 1.75.

The IR spectra of copolymers (143) and (144) are similar to those of the other styrene copolymers prepared with a carbonyl stretch at 1729 cm^{-1}, confirming the incorporation of the electroactive monomer.

The ^{1}H-NMR spectrum has serious overlapping in both the aromatic region and in the range below 2ppm. However the peaks at 3.42 (O-methylene), 3.00 (N-methylene) and 2.70ppm (N-methyl) confirmed the incoporation of the acrylate unit in the copolymer.

The ^{13}C-NMR spectrum provides the best confirmation of the structure of copolymer (143), and is assigned in table 3.12. The assignments are supported by the DEPT-135 spectrum and the C-H correlation spectrum.

Table 3.12 Assignment of the ^{13}C-NMR spectrum of copolymer (143) from 4-(p-dimethylamino-N-methylanilino)butyl acrylate (104) and styrene (composition, 10%)

^{13}C-NMR (ppm)	DEPT-135	carbons	unit A*	unit B*
23.22	negative	CH_2	$-CH_2-C-N$	
25.21	negative	CH_2	$-CH_2-C-O$	
39.25	positive	CH_3	-NMe	
40.44	positive	CH	backbone	backbone
42.23	positive	CH_3	$-NMe_2$	
43.90	negative	CH_2		backbone
45.95	negative	CH_2	backbone	
53.84	negative	CH_2	$-CH_2N-$	
63.77	negative	CH_2	$-CH_2O-$	
115.27	positive	CH	aromatic	
115.70	positive	CH	aromatic	
125.57	positive	CH		aromatic
125.72	positive	CH		aromatic
127.51	positive	CH		aromatic
127.71	positive	CH		aromatic
128.04	positive	CH		aromatic
142.50	none	C	aromatic	
143.75	none	C	aromatic	
145.27	none	C		aromatic
176.21	none	C	carbonyl	

*Unit A: repeat unit derived from 4-(p-dimethylamino-N-methylanilino)butyl acrylate

Unit B: repeat unit derived from styrene

3.3 Experimental section

3.3.1 General

NMR spectra were recorded in deuteriochloroform on a Bruker AC-400 instrument operating at 400MHz for ^{1}H-NMR, and 100MHz for ^{13}C-NMR.

Infrared spectra were recorded on a Perkin-Elmer 983G Infrared spectrophotometer. Polymers were dissolved in chloroform and coated on a sodium chloride plate which dried under vacuum at room temperature for two hours before measurement of the spectrum.

Ultra-violet absorption spectra were recorded on a Hewlett Packard 8452A diode array UV-Visible spectrophotometer.

Elemental analyses were carried out by the Microanalytical Laboratory, University College Dublin.

3.3.2 Gel Permeation Chromatography

GPC was carried out using a PL-GEL (10μm MIXED 300 x 7.5mm) column, and a PL-GEL (10μm 100A 50 x 7.5mm) pre-column. A 20μl injection loop was used. The detector was a Waters R401 Differential Refractometer. The method of Universal Calibration (section 3.1.4) was used to determine the molecular weights of the polymers. For the copolymers with methyl acrylate and the homopolymers, poly(methyl methacrylate) standards (Polymer Laboratories Ltd.) were used for the calibration curve; for the copolymers with styrene, polystyrene standards (Polymer Laboratories Ltd.) were used. Tetrahydrofuran (THF) was used as the mobile phase (flow rate 0.4cm^3/min), and toluene as the internal standard to correct for deviation in flow rate. The mobile phase was degassed by filtering through 0.5μm Millipore filters under vacuum. Standards and samples were prepared in THF at concentrations of 2g/l. The data from the detector was analysed (section 3.1.4) using GPC software (Polymer Laboratories Ltd.) on a BBC microcomputer.

3.3.3 Purification of AIBN[151]

AIBN was used as initiator in all the free radical polymerizations and was purified before use. A saturated solution of AIBN in methanol at room temperature was prepared and then cooled in a refrigerator to -5°C. The crystals were collected on a fritted-glass filter after 10 hours and were dried under vacuum at room temperature.

3.3.4 Purification of methyl acrylate[152]

Because commercially available monomers contain inhibitors to prevent polymerization during transport and storage, it is necessary to purify the monomer before polymerization. The chemical grade (BDH) methyl acrylate used contained 0.02% 4-methoxyphenol as inhibitor. Before use this inhibitor was removed by washing with 10% aqueous sodium hydroxide. Roughly equal parts of the basic solution and the monomer were placed in a separatory funnel and mixed by tumbling. The heavier aqueous phase was drained off. The procedure was repeated twice. The monomer was then washed with distilled water until litmus paper showed that all the base had been removed. The methyl acrylate was dried over anhydrous sodium sulphate (100g/l), then distilled under reduced pressure with nitrogen protection.

3.3.5 Purification of styrene[151]

The stabilizer in chemical grade styrene (Merck) is 4-tert-butylpyrocatechol (20ppm) and purification was carried out using the following procedure. The styrene was washed with 10% aqueous sodium hydroxide. Roughly equal parts of the basic solution and the monomer were placed in a separatory funnel and mixed by tumbling. The heavier aqueous phase was drained off. The procedure was repeated twice. The monomer was then washed with distilled water until litmus paper showed that all the base had been removed. The styrene was dried over anhydrous sodium sulphate (100g/l), then was distilled under reduced pressure with nitrogen protection.

3.3.6 Attempted anionic polymerization of 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98)

(a) Initiation with sodium naphthalene

Naphthalene was purified by resublimation at 70^{o}C and dried under vacuum. Tetrahydrofuran (THF) was heated under reflux over calcium hydride for 30 minutes, then distilled, and stored over calcium hydride.[153]

Purified THF (17cm^3), purified naphthalene (0.5g) and metallic sodium (0.5g, cut into small pieces) were placed in a flask equipped with a stirring bar. The flask was purged with dry nitrogen, and the nitrogen pressure was maintained slightly above atmospheric. Dark green sodium naphthalide had formed after five minutes, then the solution was stirred for another two hours.

2-(p-Dimethylamino-N-methylanilino)ethyl methacrylate toluenesulphonic acid salt (99) (0.52g) was treated with aqueous sodium hydroxide aqueous solution (3cm^3, 1.3M), and extracted with diethyl ether (5cm^3). The ether layer was washed with water three times (5 cm^3 each time), then dried first with anhydrous magnesium sulphate then with sodium metal and calcium hydride.

To a 10cm^3 predried flask equipped with a magnetic stirrer was added the dried ether solution containing 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98) and dried THF (5cm^3). The flask was sealed with a suba-seal, a long syringe needle was used as a dry nitrogen inlet , and a short one protected with a drying tube, as an outlet. This flask was placed in a cold bath containing a mixture of five parts of calcium chloride hexahydrate and four parts of crushed ice. After stirring for 10 minutes, the temperature of the reaction mixture fell to -40°C, and $0.1cm^3$ of sodium naphthalide solution was injected. The green sodium naphthalide colour was discharged and the reaction mixture developed a yellow colour. After five hours reaction, the reaction mixture was poured into light petroleum (b.p. 40 - 60°C) ($50cm^3$), however no precipitate formed, suggesting no polymer was formed.

(b) Initiation with ethyl magnesium bromide

Magnesium turnings (0.5g), anhydrous diethyl ether ($7cm^3$) and ethyl bromide ($3.2cm^3$) were added to a predried $10cm^3$ round bottom flask which was equipped with a condenser protected by a drying tube. The reaction was allowed to proceed until effervescence ceased.

2-(p-Dimethylamino-N-methylanilino)ethyl methacrylate toluene sulphonic acid salt (99) (0.52g) was treated with aqueous sodium hydroxide solution (1.3M, $3cm^3$), and extracted with diethyl ether ($5cm^3$). The diethyl ether layer was dried first with anhydrous magnesium sulphate then with sodium metal and calcium hydride.

All the dried diethyl ether solution obtained from the previous step containing 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98) was injected into a $5cm^3$ flask sealed with a suba-seal, and ethyl magnesium bromide in diethyl ether solution ($0.5cm^3$) was injected. Under nitrogen protection it was stirred at room temperature for 5 hours, No precipitate formed in the diethyl ether solution. When the diethyl ether solution was poured into light petroleum (b.p. 40 - 60°C) ($30cm^3$), no polymer precipitated.

3.3.7 Synthesis of poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130)

2-(p-Dimethylamino-N-methylanilino)ethyl methacrylate toluenesulphonic acid salt (99) (1.68 g) was placed in a test tube, aqueous sodium hydroxide solution (1.3M, 5cm^3) was added. The monomer (98) was extracted with ethyl acetate (4cm^3). The ethyl acetate layer was washed once with distilled water (4cm^3). It was placed in a 5cm^3 round bottom flask containing purified AIBN (4mg) and equipped with a condenser, a magnetic stirrer, and nitrogen inlet. A bubbler was used to maintain a slight positive pressure of nitrogen gas. An oil bath was used to regulate the reaction temperature to 75^{o}C. After 7 hours stirring, the viscous solution was cooled to room temperature and nitrogen protection was removed. The solution was poured into light petroleum (b.p.40 - 60^{o}C) (20cm^3) with stirring. Polymer obtained as a precipitate from the light petroleum was collected and dried under vacuum. It was then dissolved in ethyl acetate and precipitated in light petroleum again. This dissolution and precipitation process was carried out a total of three times. Finally the polymer (0.43 g, 42%) was dried under vacuum at room temperature for 20 hours.

UV/Vis (chloroform): λ_{max} 275 (ε, 28,400), and 330 (sh.,3,720)nm.

IR: ν_{max} 2947, 2883, 2793, 1727 (C=O), 1613, 1518, 1477, 1447, 1329, 1269, 1210, 1153, 1060, 1026, 993, 948, 907, 812, 751, and 653 cm^{-1}.

^{1}H-NMR (see fig. 3.6): δ 0.85 (broad s), 1.00 (broad s), 1.75 (broad s), 1.83 (broad s), 2.80 (s, 9H, NMe), 3.40 (s, 2H, NCH$_2$), 4.02 (s, 2H, OCH$_2$), 6.77ppm (s, 4H, Ar-H). Integration of the 0.6 - 1.4ppm region showed three protons. Integration of the 1.5 - 2.2ppm region showed two protons.

The COSY spectrum confirmed coupling between the peaks at 3.40ppm and the peak at 4.02ppm.

^{13}C-NMR (see fig. 3.7): 16.76 (α–Me), 18.66 (α–Me), 39.28 (NMe), 42.20 (NMe), 44.67 (α–C), 45.07 (α–C), 51.83 (NCH_2), 54.36 (broad) (β–CH_2), 62.61 (OCH_2), 114.65 (aromatic), 115.72 (aromatic), 142.29 (aromatic), 149.43 (aromatic), 176.57 (carbonyl), 177.36 (carbonyl), and 177.75 (carbonyl)ppm.

DEPT-135 spectrum (see fig. 3.7): 16.76 (positive), 18.66 (positive), 39.28 (positive), 42.20 (positive), 51.83(negative), 54.36 (broad) (negative), 62.61 (negative), 114.65 (positive), and 115.72 (positive)ppm

C-H correlation spectrum: confirmed coupling between the peak at 2.80ppm in the ^{1}H-NMR and the peaks at 39.28 and 42.20ppm in the ^{13}C-NMR spectrum, also coupling between the peak at 6.77ppm in the ^{1}H-NMR and the two peaks at 114.65 and 115.72ppm in the ^{13}C-NMR spectrum.

Found: C, 68.76; H, 8.59; N, 10.47%. $C_{15}H_{22}N_2O_2$ requires C, 68.67; H, 8.45; N, 10.68%.

GPC: PMMA standard samples were used for determination of the calibration curve. The molecular weight values obtained from duplicate determinations for (130) were: (i) $\bar{M}_w$ = 52,800, $\bar{M}_n$ = 16,100, $\bar{M}_z$ = 115,000, $\bar{M}_w/\bar{M}_n$ = 3.27 and (ii) $\bar{M}_w$ = 54,800, $\bar{M}_n$ = 18,900, $\bar{M}_z$ = 117,000, $\bar{M}_w/\bar{M}_n$ = 2.89.

3.3.8 Synthesis of poly[2-(p-dimethylamino-N-methylanilino)ethyl acrylate] (131)

2-(p-Dimethylamino-N-methylanilino)ethyl acrylate toluenesulphonic acid salt (102) (1.70g) was placed in a small test tube, aqueous sodium hydroxide solution (1.3M, 5cm^3) was added to liberate monomer (101). Two phases formed in the test tube. The top layer of monomer (101) was separated from the bottom layer and washed twice with distilled water (2cm^3 each time). This monomer (101) was placed in a 5cm^3 flask containing purified AIBN (4.5mg) and equipped with a nitrogen inlet, a magnetic stirrer, a condenser, an oil bath and a bubbler. The monomer was purged with nitrogen for five minutes then the pressure was adjusted to slightly higher than the external atmosphere. The temperature was raised at 80°C and the reaction mixture stirred for 9 hours. The viscous mixture was cooled to room temperature. Ethyl acetate ($3cm^3$) was added to dissolve the product in the flask. Polymer (131) was precipitated by pouring this solution into light petroleum (b.p.40 - 60°C) ($50cm^3$). This dissolution and precipitation was repeated three times, then the polymer (131) (0.32g, 29%) was dried under vacuum for 20 hours at room temperature.

UV/Vis (chloroform) λ_{max} 280 (ε, 27,500), and 330 (sh., 3,800) nm.

IR: ν_{max} 3049, 2949, 2879, 2793, 1731(C=O), 1614, 1518, 1476, 1448, 1393, 1329, 1209, 1166, 1058, 990, 948, 910, 812, 731, and $652cm^{-1}$.

^{1}H-NMR δ 1.25, 1.42, 1.62, 1.87, 2.18, 2.34, 2.79 (s, 9H, NMe), 3.38 (s, 2H, OCH_2), 4.12 (s, 2H, OCH_2), and 6.70 (s, 4H, Ar-H). Integration of the 1.1 - 2.1ppm region shows two protons. Integration of the 2.1- 2.6ppm region shows one proton.

^{13}C-NMR 35.21(broad) (β-CH_2), 39.34 (NMe), 41.43 (α-CH), 42.52 (NMe), 51.95 (NCH_2), 61.85 (OCH_2), 114.40 (aromatic), 116.09 (aromatic), 142.70 (aromatic), 143.85 (aromatic), and 174.13 (carbonyl)ppm.

DEPT-135 35.21 (broad) (negative), 39.34 (positive), 41.43 (positive), 42.52 (positive), 51.95 (negative), 61.85 (negative), 114.40 (positive), and 116.09 (positive)ppm.

Found: C, 67.42; H, 8.02; N, 11.25% . $C_{14}H_{20}N_2O_2$ requires C, 67.70; H, 8.12; N 11.29%.

GPC: (i) $\overline{M}_w$ = 42,000, $\overline{M}_n$ = 21,400, $\overline{M}_z$ = 64,000, $\overline{M}_w/\overline{M}_n$ = 1.96 and (ii) $\overline{M}_w$ = 47,800, $\overline{M}_n$ = 25,400, $\overline{M}_z$ = 67,200, $\overline{M}_w/\overline{M}_n$ = 1.88.

3.3.9 Synthesis of poly[4-(p-dimethylamino-N-methylanilino)butyl acrylate] (132)

4-(p-Dimethylamino-N-methylanilino)butyl acrylate 3,5-dinitrobenzoic acid salt (105) (2.53g) was placed in a small test tube, aqueous sodium hydroxide solution (1.3M, 10cm^3) was added to liberate monomer (104). Two phases formed in the test tube. The top layer of monomer (104) was separated from the bottom layer and was washed twice with distilled water (2cm^3 each time). This monomer (104) was placed into a 5cm^3 flask containing purified AIBN (4.5 mg), and equipped with a nitrogen inlet, a magnetic stirrer, a condenser, an oil bath and a bubbler. The reaction mixture was purged with nitrogen for five minutes then the pressure was adjusted to slightly higher than the external atmosphere. The temperature was raised to 80^{o}C and the reaction mixture strongly stirred. After 8 hours polymerisation, the viscous mixture was cooled to room temperature. Ethyl acetate (3cm^3) was added to dissolve the product in the flask. Polymer (132) was precipitated by pouring this solution into light petroleum (b.p. 40 - 60^{o}C) (50cm^3). This dissolution and precipitation were repeated three times, then the polymer (132) (0.23g, 22%) was dried under vacuum for 20 hours at room temperature.

UV/Vis (chloroform) λ_{max} 275 (ε, 28,700), and 330 (sh., 3,700) nm.

IR: ν_{max} 2950, 2796, 1730 (C=O), 1616, 1518, 1451, 1343, 1269, 1166, 1070, 948, 813, 724, and 714cm^{-1}.

^{1}H-NMR: δ 1.30 (broad), 1.62 (broad), 1.96 (broad), 2.31 (s, broad, 1H), 2.86 (s, 9H, NMe), 3.18 (s, 2H, NCH$_2$), 4.02 (s, 2H, OCH$_2$), 6.72 (s, 4H, Ar-H).

Integration of the1.1 - 2.1ppm region shows six protons. There are one major peak at 1.62ppm and two smaller peaks at 1.30 and 1.96ppm in this region.

COSY: the peak at 1.4 - 1.7ppm is correlated with the peak at 3.18ppm, 4.02ppm and 2.31ppm.

^{13}C-NMR: 23.07 (CH_2), 26.24 (CH_2), 35.00 (β-CH_2) 39.65 (NMe), 41.34 (α-CH), 42.41 (NMe), 53.95 (NCH_2), 64.46 (OCH_2), 115.44 (aromatic), 115.98 (aromatic), 142.26 (aromatic), 142.89 (aromatic), and 174.25 (carbonyl)ppm.

Found C, 69.80; H, 8.61; N, 9.98%. $C_{16}H_{24}N_2O_2$ requires C, 69.52; H, 8.76; N, 10.14%.

GPC: (i) M_w =80,500 , M_n =34,800, M_z =141,000 , M_w/M_n =2.30 and (ii) M_w =77,900 , M_n =32,600, M_z = 133,000 , M_w/M_n = 2.39.

3.3.10 Synthesis of copolymers of 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate (98) with methyl acrylate

(a) Copolymer (approximately 10%) (133)

2-(p-Dimethylamino-N-methylanilino)ethyl methacrylate toluenesulphonic acid salt (99) (0.6g, 1.4 x 10^{-3}mol) was placed in a test tube, aqueous sodium hydroxide solution (1.3M, 4cm^3) was added.The monomer (98) was extracted with ethyl acetate (2cm^3). The ethyl acetate layer was washed once with distilled water (2cm^3). This ethyl acetate solution of the liberated monomer (98) and purified methyl acrylate (0.94g, 1.09 x 10^{-2}mol) were placed in a 5cm^3 round bottom flask containing purified AIBN (3mg) and equipped with a condenser, a magnetic stirrer, and nitrogen inlet. A bubbler was used to maintain a slight positive pressure of nitrogen gas. An oil bath was used to regulate the reaction temperature to 75°C. After 11 hours stirring, the viscous solution was cooled to room temperature and nitrogen protection was removed. The solution was poured into light petroleum (b.p. 40 - 60°C) ($20cm^3$). Polymer obtained as a precipitate from the light petroleum was collected and dried under vacuum. It was then dissolved in ethyl acetate ($3cm^3$) and precipitated in light petroleum (40 - 60°C) ($20cm^3$) again. This dissolution and precipitation was carried out a total of three times. Finally the polymer (133) (0.81g, 61%) was dried under vacuum at room temperature for 20 hours.

IR (see fig. 3.8): ν_{max} 2955, 2793, 1737, 1518, 1446, 1338, 1190, 1166, 1056, 960, 940, 825, and $757cm^{-1}$.

^{1}H-NMR: δ 0.88, 1.00, 1.07, 1.12, 1.67, 1.90, 2.30, 2.84 (NMe), 2.90 (NMe), 3.50 (NCH_2), 3.57 (OMe), 3.62 (OMe), 4.12 (OCH_2), and 6.78 (Ar-H)ppm. Composition calculated from the ^{1}H-NMR spectrum is 11%

Calculation of composition from ^{1}H-NMR spectrum: A is the integration of peak at 6.78ppm from aromatic protons; B is the integration for peaks at 3.62 and 3.57 from OMe. n is the number of electroactive monomer units in the copolymer, m is the number of methyl acrylate. From equations $4n = A$ and $3m = B$, the n and m value were derived. Composition of the copolymer is $[n/(n+m)]100\%$.

The COSY spectrum confirmed coupling between peaks at 3.50 and 4.12ppm, and peaks between 1.67 and 2.30ppm.

^{13}C-NMR (see fig. 3.9): 19.92, 20.43, 34.18, 34.86, 35.06, 35.42, 37.13, 39.15 (NMe), 41.07, 41.21, 42.10 (NMe), 45.14, 51.60 (OMe), 62.16, 114.58, 115.69, 142.30, 143.50, 174.78, 175.28, 175.59, and 175.80ppm;

DEPT-135: 19.92 (positive), 20.43 (positive), 34.18 (negative), 34.86 (negative), 35.06 (negative), 35.42 (negative), 37.13 (negative), 39.15 (positive), 41.07 (positive), 41.21 (positive), 42.10 (positive), 51.60 (positive), 51.68 (negative), 62.16 (negative), 114.58 (positive), and 115.69 (positive)ppm.

C-H correlation confirmed coupling between the peak at 3.62ppm in the ^{1}H-NMR and the peak at 51.60ppm in the ^{13}C-NMR., coupling between the peak at 2.84ppm and the peak at 42.10ppm in the ^{13}C-NMR, and the coupling between the peak at 2.30 in ^{1}H-NMR spectrum and the peaks at 41.21 and 41.07ppm in the ^{13}C-NMR spectrum.

Found C, 59.63; H, 9.58; N, 3.31%. The composition of the copolymers was defined as the percentage of the electroactive monomer unit in the polymer. The composition of this copolymer (133) calculated from microanalysis results was 11%.

Calculation of composition from elemental microanalysis: n is the average number of electroactive monomer units in the copolymer, m is the average number of methyl acrylate monomer units in the copolymer. Nitrogen content is A, carbon content is B. From equations 2X14n = A and 15X12n+4X12m = B, n and m value can be derived, hence the composition.

GPC: (i) $\overline{M}_w$ = 111,000 , $\overline{M}_n$ = 56,200, $\overline{M}_z$ = 179,000, $\overline{M}_w/\overline{M}_n$ =1.98 and (ii) $\overline{M}_w$ = 115,000, $\overline{M}_n$ = 54,400 , $\overline{M}_z$ = 199,000 , $\overline{M}_w/\overline{M}_n$ = 2.11.

(b) Copolymer (approximately 5%) (134)

The procedure for the preparation of 5% copolymer (134) was similar to the one described above for (133).

Initiator: AIBN (4mg); Solvent: ethyl acetate (3cm^3); polymerization temperature: 75^{o}C; polymerization time: 4 hours; 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate toluenesulphonic acid salt (99) (0.27g, 6.1 x 10^{-4}mol); methyl acrylate (1.00g, 1.16 x 10^{-2} mol). The conversion of monomer (98) into polymer (134) was: 0.80g, 68%.

IR: ν_{max} 2956, 2927, 2855, 1736, 1518, 1446, 1379, 1331, 1197, 1166, 1123, 975, 826, and 759 cm^{-1}.

^{1}H-NMR: δ 0.90, 1.00, 1.05, 1.43, 1.62, 1.90, 2.30, 2.85, 3.41, 3.60, 4.06, and 6.75ppm. Composition calculated from the ^{1}H-NMR spectrum is 5%.

^{13}C-NMR: 19.90, 20.40, 34.20 - 35.76 (broad), 37.13, 39.23 (NMe), 41.10, 41.25, 42.15 (NMe), 45.15, 51.70 (OMe), 62.34, 114.50, 115.69, 142.30, 143.50, 174.80, 175.30, 175.58, and 175.80ppm;

Found: C, 57.31; H, 7.48; N, 1.59%. The composition of this copolymer (134) calculated from microanalysis result is 5%.

GPC: (i) $\bar{M}_w$ = 105,000, $\bar{M}_n$ = 26,300, $\bar{M}_z$ = 227,000, $\bar{M}_w/\bar{M}_n$ = 4.00, and (ii) $_w$ = 104,000, $\bar{M}_n$ = 32,900 , $\bar{M}_z$ = 216000, $\bar{M}_w/\bar{M}_n$ = 3.10.

3.3.11 Copolymers of 2-(p-dimethylamino-N-methylanilino)ethyl acrylate with methyl acrylate

(a) Copolymer (approximately 10%) (135)

The synthesis procedure is similar to that described in section 3.3.10(a). Initiator: AIBN (3mg); Solvent: benzene (3cm^3); polymerization temperature: 75^{o}C; polymerization time: 8 hours; 2-(p-dimethylamino-N-methylanilino)ethyl acrylate toluenesulphonic acid salt (102) (0.6g, 1.5 x 10^{-3}mol); methyl acrylate (0.9g, 1.1 x 10^{-2}mol). Yield was 0.74g, 57%.

IR: ν_{max} 2954, 1732 (C=O), 1518 (Ar.), 1446, 1330, 1166, 1058, 827, and 758 cm^{-1}.

^{1}H-NMR (see fig. 3.10): δ 1.49, 1.65, 1.94, 2.30, 2.85 (NMe), 3.45, 3.70 (OMe), 4.20, and 6.70 (ArH)ppm. Composition calculated from the ^{1}H-NMR spectrum is 10%.

The COSY spectrum confirmed the coupling between the peak at 1.49ppm and the peak at 1.94 ppm, the coupling between the peak at 1.65 ppm and the peak at 2.30ppm, and the coupling between the peak at 3.45ppm and the peak at 4.20ppm.

^{13}C-NMR (see fig. 3.11): 34.87, 35.08, 35.46, 39.33(NMe), 41.05, 41.21, 42.06 (NMe), 51.71 (OMe), 52.08, 61.86, 114.62, 115.59, 142.05, 143.67, 174.33, and 174.83ppm.

DEPT-135 (see fig. 3.11): 34.87 (negative) , 35.08 (negative), 35.46 (negative), 39.33 (positive), 41.05 (positive), 41.21 (positive), 42.06 (positive), 51.71 (positive), 52.08 (negative), 61.86 (negative), 114.62 (positive), and 115.59 (positive)ppm.

C-H correlation spectrum confirmed the coupling between peak at 3.70ppm in the ^{1}H-NMR and the peak at 51.71ppm in the ^{13}C-NMR; the coupling between the peak at 2.30ppm in the ^{1}H-NMR and peaks at 41.21 and 41.05ppm in the ^{13}C-NMR; and the coupling between the peaks 1.49, 1.65, 1.95,ppm in the ^{1}H-NMR and the peaks at 34.87, 35.08 and 35.46ppm in the ^{13}C-NMR.

Found C, 58.89; H, 7.68; N, 2.96%. The composition of this copolymer (135) calculated from microanalysis result is 11%.

GPC: (i) $\overline{M}_w$ = 105,000, $\overline{M}_n$ = 38,000, $\overline{M}_z$ = 198,000, $\overline{M}_w/\overline{M}_n$ = 2.76, and (ii) $_w$ = 99,000, $\overline{M}_n$ = 36,600, $\overline{M}_z$ = 186,000, $\overline{M}_w/\overline{M}_n$ = 2.70.

(b) Copolymer (approximately 5%) (136)

The synthesis procedure was similar to that described in section 3.3.10(a). Initiator: AIBN (4mg); Solvent: benzene (3cm^3); polymerization temperature: 75^{o}C; polymerization time: 4 hours; 2-(p-dimethylamino-N-methylanilino)ethyl acrylate toluenesulphonic acid salt (102) (0.3g, 6.1x10^{-4}mol); methyl acrylate (1.0g, 1.2 x 10^{-2}mol). Yield was 0.78g, 65%.

IR: ν_{max} 2955, 1737 (C=O), 1518 (Ar.), 1438, 1379, 1333, 1198, 1166, 1121, 1060, 977, 827, and 758 cm^{-1}.

^{1}H-NMR: δ 1.50, 1.65, 1.95, 2.30, 2.85 (NMe), 3.45, 3.70 (OMe), 4.20, and 6.70 (ArH)ppm. Composition calculated from the ^{1}H-NMR spectrum is 5%.

^{13}C-NMR: 34.88, 35.10, 35.45, 39.30(NMe), 41.00, 41.22, 42.08 (NMe), 51.69 (OMe), 52.08, 61.86, 114.63, 115.60, 142.05, 143.67, 174.34, and 174.82ppm.

Found C, 56.70; H, 7.27; N, 1.32%. The composition of this copolymer (136) calculated from microanalysis result is 5%.

GPC: (i) $\overline{M}_w$ = 70,000, $\overline{M}_n$ = 37,900, $\overline{M}_z$ = 111,000, $M_w/\overline{M}_n$ = 1.84. (ii) $\overline{M}_w$ = 68,800, $\overline{M}_n$ = 28,800, $\overline{M}_z$ = 99,700, $\overline{M}_w/\overline{M}_n$ = 2.17.

3.3.12 Copolymers of 4-(p-dimethylamino-N-methylanilino)butyl acrylate (104) with methyl acrylate

(a) Copolymer (approximately 15%) (137)

The synthesis procedure was similar to that described in section 3.3.10(a). Initiator: AIBN (4mg); Solvent: benzene (3cm^3); polymerization temperature: 75^{o}C; polymerization time: 9 hours; 4-(p-dimethylamino-N-methylanilino)butyl acrylate 3,5-dinitrobenzoic acid salt (105) (1.8g, 2.5 x 10^{-3}mol); methyl acrylate (1.3g, 1.5 x 10^{-2}mol). Yield was 1.1g, 54%.

IR: ν_{max} 2954, 2796, 1737 (C=O), 1616, 1518 (Ar.), 1446, 1371, 1331, 1264, 1196, 1166, 1121, 1057, 948, and 816cm^{-1}.

^{1}H-NMR : δ 1.65, 1.90, 2.35, 2.75 (NMe), 3.12, 3.60 (OMe), 3.95, and 6.65 (ArH)ppm. Composition calculated from the ^{1}H-NMR spectrum is 17%.

The COSY spectrum (see fig. 3.12) confirmed the coupling between the broad peak from 1.4 to 1.7 and the peaks at 1.90, 2.35, 3.12 and 3.95ppm.

^{13}C-NMR (see fig. 3.13): 23.18, 26.25, 34.21, 34.84, 35.56, 39.15 (NMe), 40.20, 41.06, 41.28, 41.96 (NMe), 51.59 (OMe), 53.68 (NCH_2), 64.47 (OCH_2), 115.21, 115.43, 142.59, 143.60, 174.40, and 174.74ppm.

DEPT-135 (see fig. 3.13): 23.18 (negative), 26.25 (negative), 34.21 (negative), 34.84 (negative), 35.56 (negative), 39.15 (positive), 40.20 (positive), 41.06 (positive), 41.28 (positive), 41.96 (positive), 51.59 (positive), 53.68 (negative), 64.47 (negative), 115.21 (positive), and 115.43 (positive)ppm.

C-H correlation spectrum: the peak at 3.70ppm in ^{1}H-NMR correlated to the peak at 51.71ppm in the ^{13}C-NMR; the peak at 2.35ppm in the ^{1}H-NMR correlated to the peaks at 41.28 and 41.06ppm in the ^{13}C-NMR; the one at 3.60ppm in the ^{1}H-NMR correlated to the one at 51.59ppm in the ^{13}C-NMR; the one at 3.95ppm in the ^{1}H-NMR correlated to the one at 64.47ppm in the ^{13}C-NMR.

Found C, 59.92; H, 7.46; N, 4.10%. The composition of this copolymer (137) calculated from microanalysis result is 18%.

GPC: (i) $\overline{M}_w$ = 117,500, M_n = 81,000, $\overline{M}_z$ = 154,000, $\overline{M}_w/\overline{M}_n$ = 1.45, and (ii) $_w$ = 120,500, $\overline{M}_n$ = 81,600, $\overline{M}_z$ = 178,000, $\overline{M}_w/\overline{M}_n$ = 1.48.

(b) Copolymer (approximately 5%) (138)

The synthesis procedure was similar to that described in section 3.3.10(a). Initiator: AIBN (4mg); Solvent: ethyl acetate (3cm^3); polymerization temperature: 75^{o}C; polymerization time: 4.5 hours; 4-(p-dimethylamino-N-methylanilino)butyl acrylate 3,5-dinitrobenzoic acid salt (105) (0.6g, 7.9 x 10^{-4}mol); methyl acrylate (1.3g, 1.5 x 10^{-2}mol). Yield was 0.87g, 56%.

IR: ν_{max} 2955, 1737 (C=O), 1518 (Ar.), 1438, 1345, 1197, 1166, 973, 826, and 755cm^{-1}.

^{1}H-NMR : δ 1.65, 1.91, 2.36, 2.76 (NMe), 3.12, 3.62 (OMe), 3.95, and 6.65 (ArH)ppm. Composition calculated from the ^{1}H-NMR spectrum is 5%.

^{13}C-NMR: 23.17, 26.25, 34.22, 34.84, 35.56, 39.15 (NMe), 40.21, 41.05, 41.28, 41.95 (NMe), 51.60 (OMe), 53.68 (NCH$_2$), 64.47 (OCH$_2$), 115.21, 115.43, 142.58, 143.60, 174.40, and 174.74ppm.

Found C, 57.29, H, 7.40; N 1.75%. The composition of this copolymer (138) calculated from microanalysis result is 6% .

GPC: (i) M_w = 78,000, M_n = 44,500, M_z = 134,000 , M_w/M_n = 1.75, and (ii) M_w = 73,400, M_n = 37,700, M_z = 110,000, M_w/M_n = 1.94.

3.3.13 Synthesis of copolymers of 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate with styrene

(a) Copolymer (approximately 20%) (139)

2-(p-Dimethylamino-N-methylanilino)ethyl methacrylate toluenesulphonic acid salt (99) (0.87g, 2.0 x 10^{-3}mol) was placed in a test tube, aqueous sodium hydroxide solution (1.3M, 4cm^3) was added. The monomer (98) was extracted with ethyl acetate (3cm^3). The ethyl acetate layer was washed once with distilled water (2cm^3). This ethyl acetate solution containing the liberated monomer (98) and purified styrene (1.04g, 1.0 x 10^{-2}mol) were placed in a 5cm^3 round bottom flask containing purified AIBN (4mg) and equipped with a condenser, a magnetic stirrer, and nitrogen inlet. A bubbler was used to maintain a slight positive pressure of nitrogen gas. An oil bath was used to regulate the reaction temperature to 70^{o}C. After 5.5 hours stirring, the viscous solution was cooled to room temperature and nitrogen protection was removed. Polymer (139) was precipitated by pouring this solution into light petroleum (b.p. 40 - 60^{o}C) (20cm^3). After drying under vacuum at room temperature, the polymer was dissolved in ethyl acetate (3cm^3) and precipitated in light petroleum (b.p. 40 - 60^{o}C) (20cm^3) again. This dissolution and precipitation were repeated three times. Finally the polymer sample (139) (0.88g, 55%) was dried under vacuum at room temperature for 20 hours.

IR: ν_{max} 3062, 3027, 2929, 2793, 1724 (C=O), 1602, 1518, 1492, 1452, 1329, 1269, 1211, 1120, 1073, 1031, 1000, 948, 910, 811, 758, 700, and 666 cm^{-1}

^{1}H-NMR: δ 0.65, 1.60, 1.95, 2.82(NMe), 2.90, 3.80 (OCH$_2$), 6.70 (ArH), 6.90 (ArH), 7.20 (ArH)ppm. Composition calculated from the ^{1}H-NMR spectrum is 18%.

Calculation of composition from the ^{1}H-NMR spectrum: The integration for the aromatic peaks at 6.70, 6.90, and 7.20ppm is A; the integration of the peak at 3.80ppm for O-methylene is B. From equations $4n + 5m = A$ and $2n = B$, n and m value can be derived hence the composition of the copolymer.

^{13}C-NMR (see fig. 3.14): 19.50, 39.12 (NMe), 39.87, 40.39, 42.40 (NMe), 43.90, 45.33, 46.17, 46.75, 51.66, 61.75, 114.13 (Ar.), 115.90 (Ar.), 125.70 (Ar.), 127.99 (Ar.), 142.53 (Ar.), 143.17 (Ar.), 145.19 (Ar.), and 176.22 (carbonyl)ppm.

DEPT-135: 19.50 (positive), 39.12 (positive), 39.87 (positive), 40.39 (positive), 42.40 (positive), 45.33 (negative), 46.17 (negative), 46.75 (negative), 51.66 (negative), 61.75 (negative), 114.13 (positive), 115.90 (positive), 125.70 (positive), and 127.99 (positive)ppm.

Found: C, 79.57; H, 7.63; N, 3.79%. The composition of this copolymer (139) calculated from microanalysis result is 19%.

GPC: (i) $\bar{M}_w$ = 88,300 , $\bar{M}_n$ = 50800, $\bar{M}_z$ = 134,000 , $\bar{M}_w/\bar{M}_n$ = 1.74. (ii) $\bar{M}_w$ = 75,900, $\bar{M}_n$ = 44,200 , $\bar{M}_z$ = 110,000, $\bar{M}_w/\bar{M}_n$ =1.71.

(b) Copolymer (approximately 5%) (140)

The procedure for the preparation of 5 % copolymer (136) was similar to that described above for the copolymer (139). Initiator: AIBN (4mg); Solvent: ethyl acetate (2cm^3); polymerization temperature: 70^{o}C; polymerization time: 4 hours; 2-(p-dimethylamino-N-methylanilino)ethyl methacrylate toluene sulphonic acid salt (99) (0.23g, 5.3 x 10^{-4}mol); styrene (1.04g, 1.0 x 10^{-2}mol). Yield was 0.86 g, 72%.

IR: ν_{max} 3084, 3062, 3028, 2927, 2852, 1725 (C=O), 1601, 1584, 1518, 1492, 1452, 1331, 1218, 1119, 1072, 1030, 947, 908, 810, 757, 699, and 665 cm^{-1}.

^{1}H-NMR: δ 0.65, 1.62, 1.95, 2.80(NMe), 2.95, 3.89, 6.70 (ArH), 6.90 (ArH), 7.20 (ArH)ppm. Composition calculated from the ^{1}H-NMR spectrum is 8%.

^{13}C-NMR: 19.49, 39.12 (NMe), 39.88, 40.40, 42.40 (NMe), 43.90, 45.30, 46.18 46.75, 51.65, 61.75, 114.10 (Ar.), 115.90 (Ar.), 125.70 (Ar.), 128.01 (Ar.), 142.54 (Ar.), 143.16 (Ar.), 145.19 (Ar.), and 176.20 (carbonyl)ppm.

Microanalysis found C, 87.99; H, 8.52; N, 1.05%. The composition of this copolymer (140) calculated from microanalysis result is 9% .

GPC: (i) $\overline{M}_w$ = 82,500 , $\overline{M}_n$ = 45,800, $\overline{M}_z$ = 123,000 , $\overline{M}_w/\overline{M}_n$ = 1.80. (ii) $\overline{M}_w$ = 86,500, $\overline{M}_n$ = 44,700, $\overline{M}_z$ = 144,000, $\overline{M}_w/\overline{M}_n$ = 1.94.

3.3.14 Copolymers of 2-(p-dimethylamino-N-methylanilino)ethyl acrylate (101) with styrene

(a) Copolymer (approximately 15%) (141)

The synthesis procedure was similar to that described in section 3.3.13(a). Initiator: AIBN (4mg); Solvent: benzene ($3cm^3$); polymerization temperature: 70^oC; polymerization time: 5 hours; 2-(p-dimethylamino-N-methylanilino)ethyl acrylate toluene sulphonic acid salt (102) (0.85g, 2.0 x 10^{-3}mol); styrene (1.04g, 1.0 x 10^{-2}mol). Yield was 0.75g, 47%.

IR: ν_{max} 3061, 3028, 2927, 2851, 1729 (C=O), 1602, 1518, 1492, 1452, 1329, 1209, 1163, 1070, 1030, 947, 908, 811, 759, and $700cm^{-1}$

^{1}H-NMR: δ 0.75, 1.30, 1.38, 1.70, 1.91, 2.68 (NMe), 3.60, 6.52 (ArH), and 6.90 (ArH)ppm. Composition calculated from the ^{1}H-NMR spectrum is 15%.

^{13}C-NMR: 39.19, 40.43, 41.07, 42.27, 43.57, 46.50, 52.00 (NCH_2), 61.50 (OCH_2), 114.39 (Ar.), 115.93 (Ar.), 125.71 (Ar.), 127.89 (Ar.), 128.07 (Ar.), 142.12 (Ar.), 143.62 (Ar.), 145.14 (Ar.), and 175.72 (carbonyl)ppm

DEPT-135: 40.43 (positive), 41.07 (positive), 52.00 (negative), 61.50 (negative), 114.39(positive), 115.93(positive), 125.71(positive), 127.89(positive), and 128.07(positive)ppm. Other peaks in range 37 - 48ppm are not clear due to overlapping.

Found C, 83.89; H, 8.00; N, 3.21%. The composition of this copolymer (141) calculated from microanalysis result is 15% .

GPC: (i) $\overline{M}_w$ = 89,700, $\overline{M}_n$ = 53,000, $\overline{M}_z$ = 133,000 , $\overline{M}_w/\overline{M}_n$ = 1.69 and (ii) $\overline{M}_w$ = 91,200 , $\overline{M}_n$ = 50,300, $\overline{M}_z$ = 142,000, $\overline{M}_w/\overline{M}_n$ = 1.81.

(b) Copolymer (approximately 5%) (142)

The synthesis procedure was similar to that described in section 3.3.13(a) Initiator: AIBN (4mg); Solvent: benzene(3cm^3); polymerization temperature: 70^{o}C; polymerization time: 4.5 hours; 2-(p-dimethylamino-N-methylanilino)ethyl acrylate toluene sulphonic acid salt (102) (0.22g, 5.30x10^{-4}mol); styrene (1.04g, 1.00 x 10^{-2}mol). Yield was 0.81g, 69%.

IR: ν_{max} 3084, 3061, 3028, 2927, 2852, 1730 (C=O), 1601, 1583, 1518, 1492, 1452, 1329, 1219, 1157, 1070, 1029, 965, 947, 908, 811, 758, 700, and 665cm^{-1}.

^{1}H-NMR: δ 0.75, 1.40, 1.71, 1.91, 2.70 (NMe), 3.0, 3.60, 6.50 (ArH), and 6.90 (ArH)ppm. Composition calculated from the ^{1}H-NMR spectrum is 5%.

^{13}C-NMR: 39.20, 40.44, 41.07, 42.24, 43.57, 46.54, 52.00 (NCH$_2$), 61.50 (OCH$_2$), 114.40 (Ar.), 115.92 (Ar.), 125.72 (Ar.), 127.80 (Ar.), 128.04 (Ar.), 142.20 (Ar.), 143.66 (Ar.), 145.24 (Ar.), and 175.70 (carbonyl)ppm

Microanalysis found C, 88.49; H, 8.18; N, 0.9%. The composition of this copolymer (142) calculated from microanalysis result is 4% .

GPC: (i) $\overline{M}_w$ = 54,200 , $\overline{M}_n$ = 30,600, $\overline{M}_z$ = 79.100, $\overline{M}_w/\overline{M}_n$ = 1.77 , and (ii) $\overline{M}_w$ = 63,700, $\overline{M}_n$ = 28,700 , $\overline{M}_z$ = 105,000 , $\overline{M}_w/\overline{M}_n$ = 2.22.

3.3.15 Copolymers of 4-(p-dimethylamino-N-methylanilino)butyl acrylate (104) with styrene

(a) Copolymer (approximately, 10%) (143)

The synthesis procedure was similar to that described in section 3.3.13(a) Initiator: AIBN (4mg); Solvent: ethyl acetate (3cm^3); polymerization temperature: 75^{o}C; polymerization time: 7 hours; 4-(p-dimethylamino-N-methylanilino)butyl acrylate 3,5-dinitrobenzoic acid salt (105) (1.8g, 2.5 x 10^{-3}mol); styrene (1.6g, 1.5 x 10^{-2}mol). Yield was 0.99g, 42%.

IR: ν_{max} 3083, 3061, 3027, 2926, 2852, 1729 (C=O), 1601, 1583, 1517, 1492, 1452, 1371, 1219, 1182, 1156, 1071, 1029, 946, 908, 842, 758, 699, and 666 cm^{-1}.

^{1}H-NMR: δ 0.80, 1.40, 1.73, 2.70 (NMe), 3.0, 3.42, 6.40 (ArH), and 6.90 (ArH)ppm. Composition calculated from the ^{1}H-NMR spectrum is 11%.

^{13}C-NMR: 23.22, 25.21, 39.25(NMe), 40.44, 42.23 (NMe), 43.90, 45.95, 53.84, 63.77, 115.27 (Ar.), 115.70 (Ar.), 125.57 (Ar.), 125.72 (Ar.), 127.51 (Ar.), 127.71 (Ar.), 128.04 (Ar.), 142.50 (Ar.), 143.75 (Ar.), 145.27 (Ar.), and 176.21 (carbonyl)ppm

DEPT-135: 23.22 (negative), 25.21 (negative), 39.25 (positive), 40.44 (positive), 42.23 (positive), 43.90 (negative), 45.95 (negative), 53.84 (negative), 63.77 (negative), 115.27 (positive), 115.70 (positive), 125.57 (positive), 125.72 (positive), 127.51 (positive), 127.71 (positive), and 128.04 (positive)ppm.

Microanalysis found C, 89.31; H, 8.09; N, 2.60%. The composition of this copolymer (143) calculated from microanalysis result is 12%.

GPC: (i) $\overline{M}_w$ = 75,400, $\overline{M}_n$ = 41,800, M_z = 111,000 , $\overline{M}_w/\overline{M}_n$ = 1.80, and (ii) $\overline{M}_w$ = 79,300, $\overline{M}_n$ = 42,700, $\overline{M}_z$ = 125,000, $\overline{M}_w/\overline{M}_n$ = 1.86.

(b) Copolymer (approximately 5%) (144)

The synthesis procedure was similar to that described in section 3.3.13(a). Initiator: AIBN (4mg); Solvent: ethyl acetate (3cm^3); polymerization temperature: 75^{o}C; polymerization time: 5 hours; 4-(p-dimethylamino-N-methylanilino)butyl acrylate 3,5-dinitrobenzoic acid salt (105)(0.55g, 7.9 x 10^{-4} mol); styrene (1.56g 1.5 x 10^{-2}mol). Yield was 0.89 g, 50%.

IR: ν_{max} 3083, 3061, 3028, 3002, 2927, 2853, 2795, 1737 (C=O), 1602, 1583, 1517, 1492, 1452, 1372, 1329, 1241, 1157, 1116, 1047, 1030, 947, 909, 845, 811, 759, and 699 cm^{-1}.

^{1}H-NMR: δ 0.80, 1.40, 1.73, 2.75 (NMe), 3.1, 3.42, 6.40 (ArH), and 6.90 (ArH)ppm. Composition calculated from the ^{1}H-NMR spectrum is 5%.

^{13}C-NMR: 23.22, 25.22, 39.26(NMe), 40.44, 42.23 (NMe), 43.90, 45.96, 53.84, 63.77, 115.28 (Ar.), 115.71 (Ar.), 125.57 (Ar.), 125.72 (Ar.), 127.52 (Ar.), 127.71 (Ar.), 128.04 (Ar.), 142.50 (Ar.), 143.75 (Ar.), 145.27 (Ar.), and 176.21 (carbonyl) ppm

Found C, 88.73; H, 8.17; N 1.36%. The composition of this copolymer (144) calculated from microanalysis result is 6%.

GPC: (i) $\overline{M}_w$ = 94,000, $\overline{M}_n$ = 53,800, $\overline{M}_z$ = 142,000, $\overline{M}_w/\overline{M}_n$ = 1.75. (ii) $\overline{M}_w$ = 90,000, $\overline{M}_n$ = 51,400, $\overline{M}_z$ = 133,000, $\overline{M}_w/\overline{M}_n$ = 1.75.

Chapter IV

Electrochemical investigation of the polymers

4.1 Introduction

As mentioned in the introductory chapter, among the major potential applications of electroactive polymers is their use in rechargeable batteries and as modified electrodes. In the form of modified electrodes, they may be useful for electroanalysis or electrocatalysis. Their study in the form of modified electrodes provides an important technique for study of the electrochemical properties of organic materials in the solid state. In the present case, basic electrochemical studies of some electroactive polymers which have been prepared were carried out using electrodes modified, i.e. coated, with the polymers.

4.1.1 Cyclic voltammetry

Since cyclic voltammetry (CV) is the electrochemical technique that has most often been employed in these studies, it is worthwhile to consider briefly some of the aspects related to the electrochemical response of redox centres through cyclic voltammetry.

In a cyclic voltammetric experiment[154] one has an unstirred solution containing a supporting electrolyte and a redox species (in solution or on the surface). The experiment consists of cycling the potential applied at the working electrode in the solution, and measuring the resulting current, with the potential of the working electrode controlled versus a reference electrode. Cyclic voltammetry has become perhaps the most effective technique for the mechanistic study of redox systems.[5] A redox system can be characterised from the potentials of the peaks on the cyclic voltammogram and from changes caused by variations in scan rate.

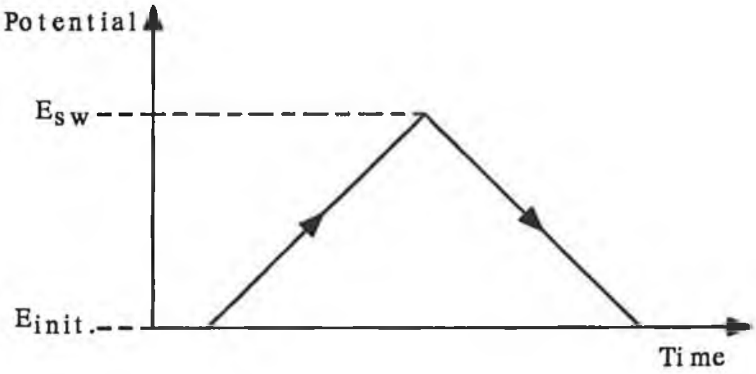


Figure 4.1 Potential excitation waveform for cyclic voltammetry

The potential waveform that is applied across the electrode/solution interface for cyclic voltammetry is illustrated in figure 4.1. Single or multiple scans may be used, and the potential scan rate can also be varied. The current evolved at the working electrode is measured during the potential scan. Typical cyclic voltammograms for a solution species and for a surface immobilized monolayer are shown in figure 4.2 and figure 4.3 respectively.

4.1.1.1 Cyclic voltammetric responses for freely diffusing species

Consider having a solution of a species Ox which can be reduced to Red with a characteristic potential $E^{0'}$ for the process. We begin by applying a potential E_{init} (A in Fig. 4.2) that is sufficiently removed from $E^{0'}$ so that essentially no current flows. We will initiate a scan in the negative direction. As the applied potential approaches $E^{0'}$ the current begins to increase (B) and continues to do so (C) until a peak (D) is reached. Upon continued scanning, the current decays in the characteristic "tailing" fashion (E). At point (F) (E_{SW}) the direction of the sweep is changed and the reverse sweep will be analogous to the forward sweep. Qualitatively we can rationalise the shape of this voltammogram by considering that early on the applied potential is so far removed from $E^{0'}$ that no current flows. In the vicinity of $E^{0'}$ we begin to reduce (Ox to Red) the material that is close to the electrode surface and at the point (D) we essentially exhaust it so that the surface concentration of Ox is zero

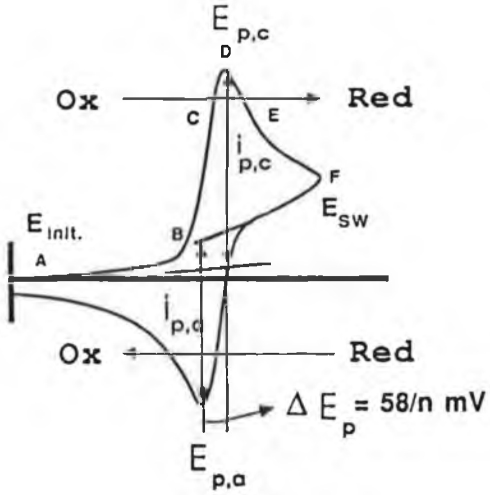


Figure 4.2 Cyclic voltammogram for a freely diffusing species

Any further material to be electrolysed needs to diffuse to the electrode surface from the solution and this gives rise to the tailing decrease in the current (often referred to as diffusional tails) The reverse sweep can be understood in analogous terms except that the process now is the re-oxidation of the reduced material that was generated in the forward sweep. In a cyclic voltammogram the parameters of importance are the peak potential ($E_{p,c}$; $E_{p,a}$) (c = cathodic, a = anodic) and current ($i_{p,c}$; $i_{p,a}$) values as well as the difference in peak potential values ΔE_p. For a chemically reversible system (that is, when Ox and Red are both chemically stable species) the ratio of peak currents will be unity at all sweep rates. For an electrochemically reversible system (that is one that is always at Nernstian equilibrium, electromotive force is linear to the logarithm of the activities of the reagents), the difference in peak potential values will be 58/n mV at 25°C (n is the number of electrons transferred). Deviations from these indicate complications, either kinetic or chemical.[154] The average of the peak potentials is taken as the formal potential ($E^{0'}$) for the redox couple. The peak current is given by the Randles-Sevcik equation:[5, 155]

$$i_p = 0.4463\,(nF)^{3/2} A D_{ct}^{1/2} C \upsilon^{1/2} / (RT)^{1/2} \qquad 4.1$$

where n is the number of electrons transferred, F is the Faraday constant, A is the electrode area, D_{ct} is the apparent transport diffusion coefficient, C is the bulk concentration and υ is the sweep rate, R is gas constant, T is absolute temperature. Thus i_p is proportional to $\upsilon^{1/2}$, C, and $n^{3/2}$.

4.1.1.2 Cyclic voltammetric responses for surface immobilized monolayers

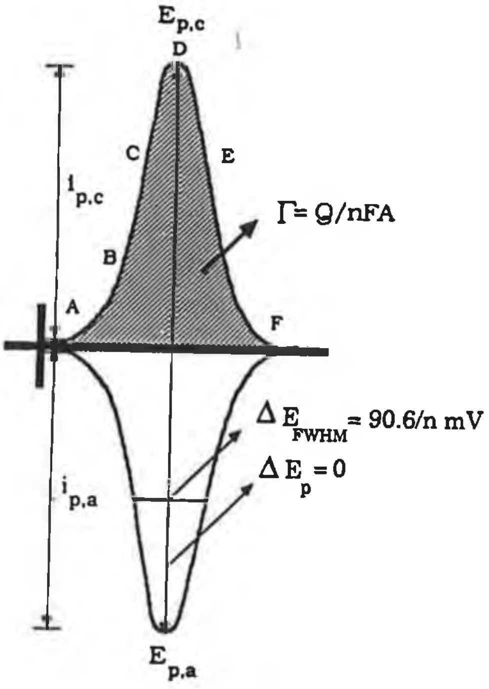


Figure 4.3 Cyclic voltammogram for a surface immobilized redox couple at monolayer coverage

The response obtained at an electrode coated with a monolayer of an electroactive material is shown in Fig. 4.3 and it is immediately apparent that the response (often referred to as a surface wave) is quite different from that previously described. We can go through an analogous analysis.

Again, at potentials far removed from $E^{0'}$ (A) no current flows. The current increases as we scan negatively (B), (C) and again a current peak (D) is observed. However, in this case the current decay (E) is just as rapid as was the increase, giving rise to a symmetrical response. The reverse scan is a mirror image of the forward scan. These differences arise from the fact that in this case there is no diffusion of electroactive material to the electrode since it is all at the electrode itself. The voltammogram shown is again for a chemically and electrochemically reversible system. As for the diffusion case, a chemically reversible system will exhibit a ratio of peak currents of 1. However, for an electrochemically reversible system the ΔE_p value will be zero with larger values (which increase with sweep rate) indicating some sluggishness in the electron transfer event. According to the theory for surface-immobilized redox centres[156, 157] if surface concentration and activity are equated, the current/potential behaviour in a cyclic voltammetric experiment for a Nernstian process is given by

$$i = [(n^2F^2\Gamma\upsilon)/(RT)][\chi/(1+\chi)^2] \qquad 4.2$$

or

$$i = 4i_p\chi/(1+\chi)^2 \qquad 4.3$$

where $\chi = \exp[(nF/RT)(E - E^0)]$, Γ = total amount of reactant initially present on the electrode surface, υ = potential sweep rate. The peak current is given by

$$i_p = n^2F^2\Gamma\upsilon/(4RT) \qquad 4.4$$

From this it follows that the peak current will be linearly dependent on the rate of potential sweep.

There are in addition other properties of surface waves that have no equivalent in the cyclic voltammetric response for diffusing species. The first one has to do with the fact that the oxidation or reduction of the surface layer represents a coulometric experiment. Thus by integrating the area under the voltammetric wave (i. e. obtaining the charge Q) one can determine the surface coverage (Γ):

$$\Gamma = Q/(nFA) \tag{4.5}$$

(Note that for most materials, monolayer will represent approximately 1 X 10^{-10} mol cm^{-2}.)

Finally, for the case of non-interacting neighbours within a film, the full width at half-maximum (FWHM) for a surface wave should be 90.6/n mV. Values larger than this reflect repulsive interactions whereas smaller values indicate attractive or stabilizing interaction[158-161] The limit of extremely sharp peaks usually indicates a phase transition.

In general, many redox couples immobilized as monolayers exhibit symmetrical wave-shapes as well as the linear dependence of peak current with rate of potential sweep.[5]

4.1.1.3 Polymer films

In the case of polymeric films on electrode surfaces a wide range of voltammetric waveshapes have been reported.[162-165] Reactions at these interfaces are much more complex than those at electrodes covered with monolayers because there are numerous aspects to be considered. Some of these include the mechanisms for electron transfer and transport through the film, especially to sites that are physically remote from the electrode surface. Also of importance are the movement of polymer chains in order to accommodate the movement of species through the film, including charge compensating ions as well as solvent molecules. The exact voltammetric waveshape is then dictated by the interplay of all of these factors.

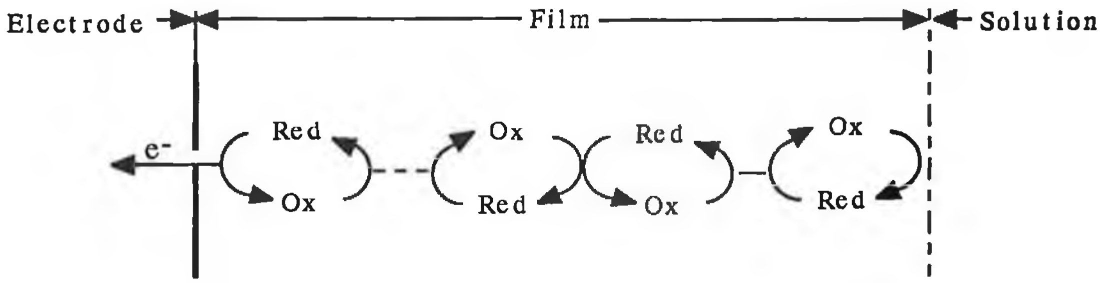


Figure 4.4 Schematic representation of electron transfer through polymer films by electron exchange between redox couples incorporated in the film. Ox and Red represent oxidized and reduced species of the redox couple, respectively.

Kaufman et al.[162] proposed a model for the transport of charge through polymer films where charge propagation takes place via electron self-exchange reactions between oxidized and reduced neighbours within the film (fig. 4.4). However, although this may represent the mechanism for the process, the overall rate (and therefore the waveshape) will be dictated by the combination of effects mentioned in the previous paragraph.

An approach that has been quite successful in the treatment of this problem is based on the fact that transport rates through these films appear to obey the laws of diffusion.[166, 167] Thus, the measurement of diffusion coefficients [variously termed D_{ct} (charge transport diffusion coefficient), D_{app} (apparent diffusion coefficient) or D_{eff} (effective diffusion coefficient)] has provided some very useful insights into these processes.

For systems with large values of D_{ct} , for low sweep rates or for sufficiently thin films, the voltammetric response will be that of a monolayer film with symmetrical waveshapes and peak currents proportional to the rate of potential sweep. For the opposite case of small D_{ct} , thick films or short experimental times, the response will revert back to that exhibited by a solution species with the characteristic diffusional tails.

In many cases one can observe the transition from a surface wave response to a diffusional wave response by simply changing the rate of potential sweep.

Therefore, cyclic voltammetry can be used to evaluate charge transport rates for modified electrodes, notably by examining the current response of the modified electrode at high sweep rate.[168] This leads to semi-infinite diffusion conditions where the depletion layer produced in the redox reaction does not extend to the film/electrolyte interfaces. These conditions leads to solution type behaviour and so established theory for solution behaviour can be used.[169]

In some instances the anodic and cathodic waveshapes can be significantly different and this is particularly prevalent in systems where one of the oxidation states of the polymer is electrically neutral. In addition, solvent effects can be dramatic in such instances.[5]

4.1.2 Methods for modifying the surface of an electrode with electroactive polymers

The investigation of polymer films on electrode surfaces is one of the most active research areas in the field of contemporary electrochemistry.[170, 171] This is partly due to the fact that the signals obtained at electrodes modified with polymer films are greatly amplified over those at monolayer coverages, thus making their measurement much easier. For catalytic applications polymer films are expected to exhibit higher stability. In addition there were theoretical predictions[172]that pointed to the advantages of polymer films (vs. monolayers) in electrocatalytic applications. In addition their use opened the way for the preparation of deliberately designed structural interfaces. Furthermore, many of the methods employed in the modification step can be very simple and include dip coating, spin coating, electropolymerization and others.

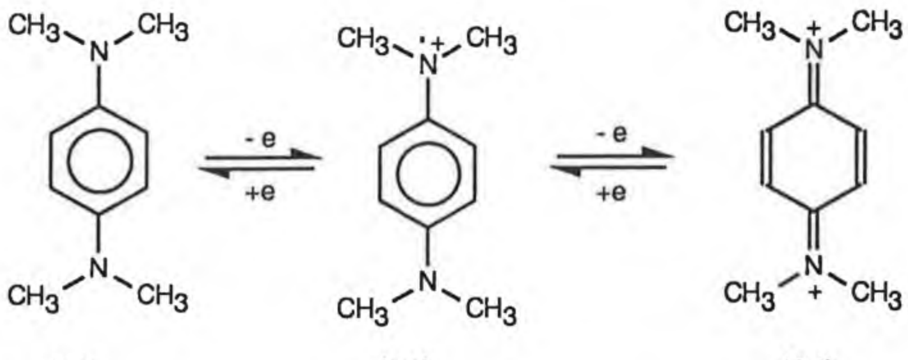
Because of the typically larger coverages involved, the electrochemical response of polymer films can be greatly complicated by the interplay of charge transfer and transport, polymer film motions, solvent swelling and others. As a result, the voltammetric responses obtained are much more difficult to interpret and in fact, a great deal of effort has been focused on the unraveling of these processes.[173,174]

The preparation of electrodes modified with redox polymers can be achieved in a number of ways. One can employ a pre-formed polymer containing the redox centre, or the redox centre can be coupled to a previously prepared polymer (e.g. by ligand substitution). They can also be generated in situ by the electroinitiated polymerization of redox active monomers. In our case, the redox centres are pendant to the polymer backbone, and the polymers are soluble in a number of common solvents, therefore they can be coated on the electrode to modify it.

4.2 Results and discussion

4.2.1 Electrochemical studies of p-dimethylamino-N,N-dimethylaniline (62)

p-Dimethylamino-N,N-dimethylaniline (62), can be oxidized and reduced electrochemically. It can be oxidized to a free radical cation (63) (the first redox couple) and then to dication (64) (the second redox couple).[90,93] The corresponding electrochemical cyclic voltammogram of this compound in acetonitrile is shown in figure 4.5



(62) (63) (64)

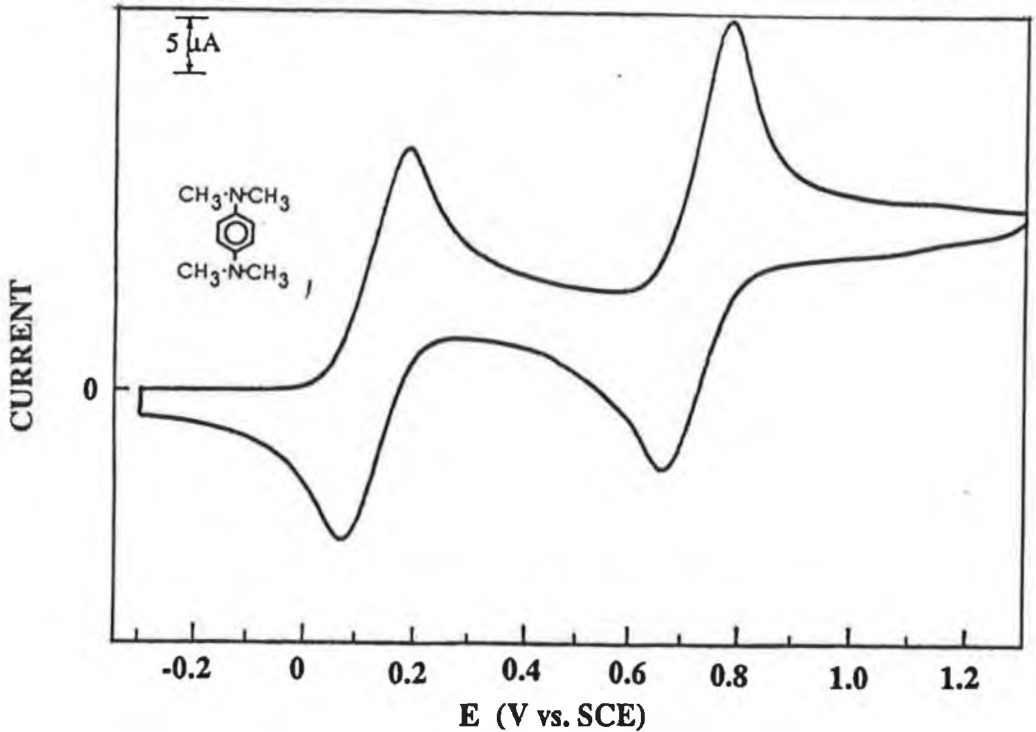
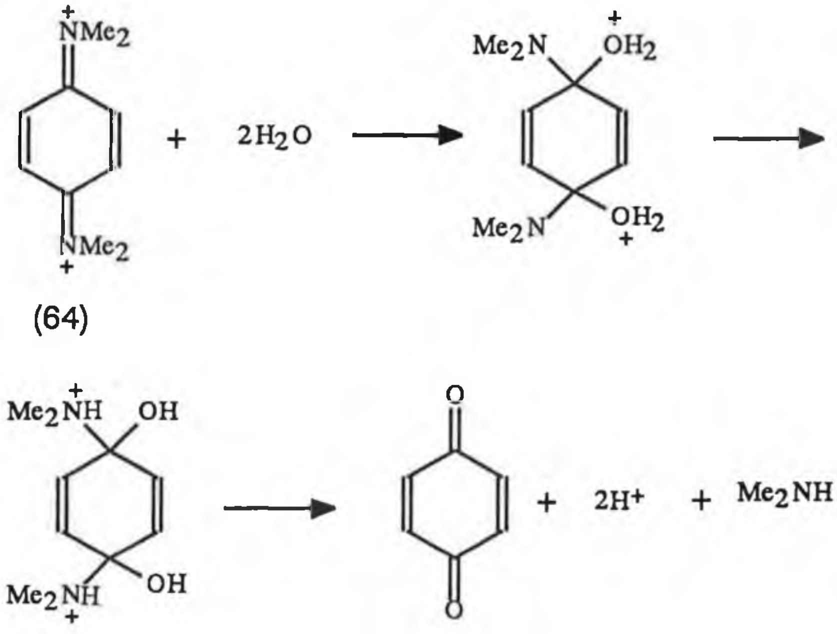


Figure 4.5 Cyclic voltammogram of p-dimethylamino-N,N-dimethylaniline (62) in 0.1M TEAP acetonitrile solution. Glassy carbon electrode. Scan rate, 50 mVs^{-1}.

In this experiment, repeated scanning from -0.3 to 0.5 V gave a stable cyclic voltammogram indicating a stable redox couple. However the cyclic voltammogram when repeatedly scanned from -0.3 to 1.3 V decreased slowly.

The radical cation was reported to be stable and has been well studied in both aqueous and acetonitrile systems,[90, 93, 175, 176] though ESR studies in aprotic[177, 179] and aqueous solvents have also indicated the stability of radical cation (63). This one electron redox couple has been widely used as a model in biological studies requiring a reversible, one--electron redox system.[93, 179, 180, 181] The radical cation salt is commercially available as Wurster Blue. The dication however reportedly decomposes in acetonitrile and aqueous systems.[90, 91, 93] However the reason for the instability of dication in acetonitrile was not clarified.[91,93]

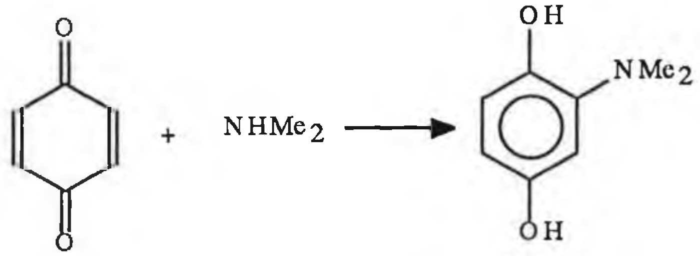
In aqueous system, the reversible CV of the first redox couple has not been reported due to the closeness of its normal potential to the second redox couple. For the second redox couple, it has been reported recently that the dication decomposes rapidly because of reaction with water.[90] The following reactions have been proposed[90] to explain complications in the electrooxidation of p-dimethylamino-N,N-dimethylaniline (62). For the diimmonium dications (64) generated after the second oxidation step, in the presence of water, deamination was proposed to produce p-benzoquinone (145) and dimethylamine (146). The reaction between p-benzoquinone (145) and dimethylamine (146) was suggested to produce an aminated hydroquinone (147) which can then be oxidized electrochemically to an aminated benzoquinone (148).



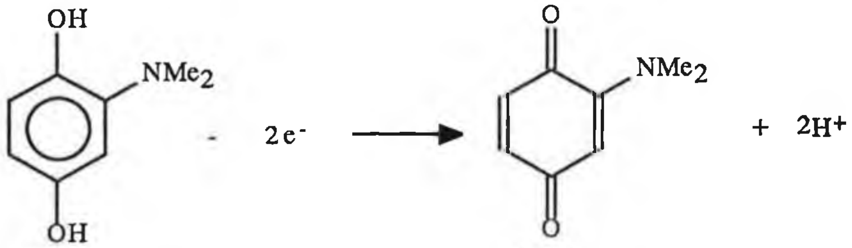
(64)

(145)

(146)



(145) (146) (147)



(147) (148)

The presence of p-benzoquinone (145), dimethylamine (146), aminated hydroquinone (147) and aminated benzoquinone (148) were deduced[90] from the cyclic voltammogram. Their peaks were assigned by comparison with the cyclic voltammograms of p-benzoquinone (145), dimethylamine (146), and aminated hydroquinone (147).

4.2.2 Cyclic voltammetric studies of the homopolymers in solution

Homopolymers poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130), poly[2-(p-dimethylamino-N-methylanilino)ethyl acrylate] (131) and poly[4-(p-dimethylamino-N-methylanilino)butyl acrylate] (132) are soluble in acetonitrile, and cyclic voltammetric studies with these polymers were carried out in this solvent with tetraethylammonium perchlorate (TEAP) as supporting electrolyte. The potential scanning range was firstly controlled from -0.3 to 0.5 V to avoid the second oxidation. Over this potential range a stable redox couple was obtained (fig. 4.6).

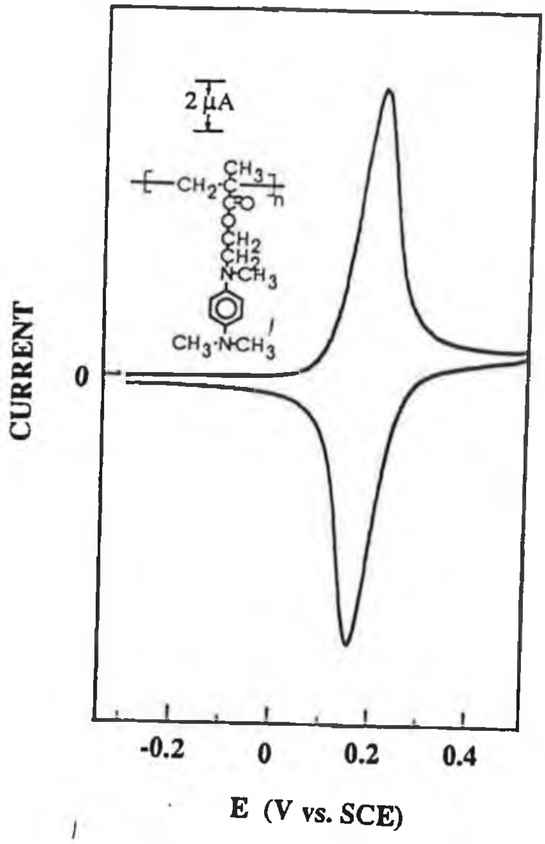


Figure 4.6 Cyclic Voltammograms of polymer (130) in 0.1 M TEAP acetonitrile solution, concentration of redox centres in the solution is 6.0 X 10^{-4}M, scan rate: 50 mVs^{-1}, glassy carbon electrode.

For each of the three polymers (130), (131), and (132) a stable redox couple was obtained. Figure 4.6 illustrates that for (130). These results show that the redox groups pendant on the polymer chains can be oxidised to their corresponding radical cations, and that a stable reversible system is observed as was seen for the non-polymeric model, p-dimethylamino-N,N-dimethylaniline (62). However the normal potentials observed for the three polymers are slightly different. Comparison of these with one another and with that of p-dimethylamino-N,N-dimethylaniline (62) showed a slight variation in electrochemical behaviour.

Table 4.1 lists the normal potential values of the first redox couple at low scanning rate in acetonitrile solution with TEAP as electrolyte.

Table 4.1 Normal potentials of the first redox couples

samples	normal potentials* vs. S.C.E.
p-dimethylamino-N,N-dimethylaniline(62)	0.11 V
poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130)	0.18 V
poly[2-(p-dimethylamino-N-methylanilino)ethyl acrylate] (131)	0.18 V
poly[4-(p-dimethylamino-N-methylanilino)butyl acrylate] (132)	0.10 V

* concentrations of redox centres in the solution were 5.0 X 10^{-4} M, scan rate 2 mV/s, glassy carbon electrode.

From table 4.1, it can be seen that the normal potentials for poly[2-(p-dimethylamino-N-methylanilino)ethyl methacrylate] (130), and poly[2-(p-dimethylamino-N-methylanilino)ethyl acrylate] (131) are higher than those for p-dimethylamino-N,N-dimethylaniline (62) and poly[4-(p-dimethylamino-N-methylanilino)butyl acrylate] (132). There are two methylene groups separating the carboxyl group from the redox active group in the structures of polymers (130) and (131), whilst there are four methylene groups separating those of polymer (132). The carboxyl group is an electron withdrawing group. Due to its inductive effect, the lone pair electrons on the nitrogen in the neutral redox group will, relative to that of p-dimethylamino-N,N-dimethylaniline (62), become somewhat more difficult to remove, as illustrated in figure 4.7.

In polymer (132) with a longer methylene chain separating the two groups, this inductive effect is weaker, therefore a lower potential is needed to remove an electron. The normal potential for polymer (132) is essentially the same as that of p-dimethylamino-N,N-dimethylaniline (62) within experimental error indicating that separation by four methylene groups has eliminated this effect.

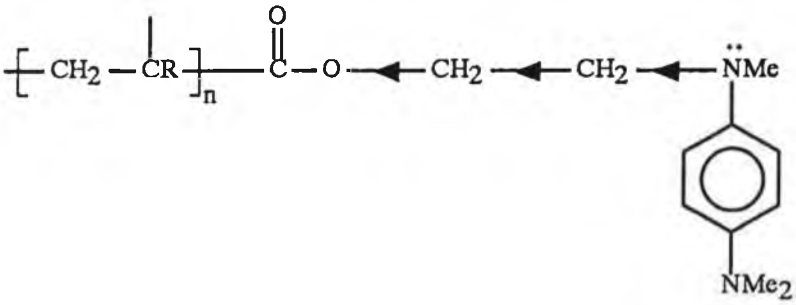


Figure 4.7 Inductive effect in polymer (130) and polymer (131)

In general however, the electrochemical behaviour of the first redox couple for the three homopolymers and for p-dimethylamino-N,N-dimethylaniline (62) is very similar except for this slight difference in normal potentials.

However, If the potential scanning range was extended to 1.3 V, the cyclic voltammograms of the homopolymers (130), (131) and (132) in solution showed two redox couples (for example, fig. 4.8) in the first scan.

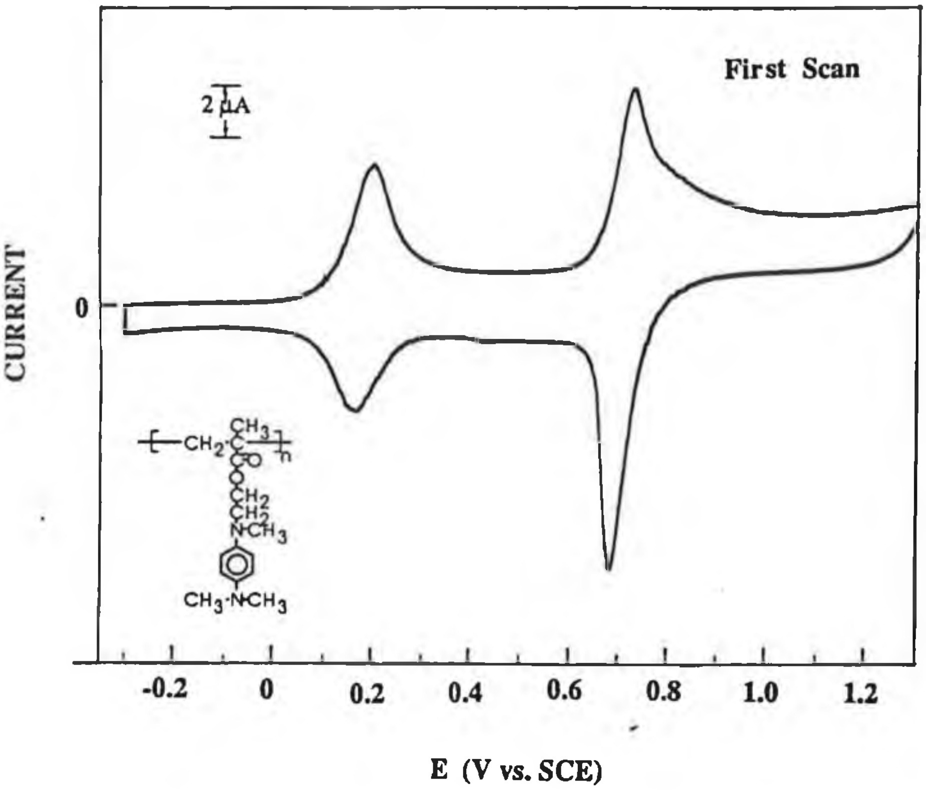


Figure 4.8 Cyclic Voltammogram of polymer (130) in 0.1 M TEAP acetonitrile solution, concentration of redox centres in the solution is 5.0×10^{-4} M, scan rate: 50 mVs^{-1}, glassy carbon electrode; first scan.

The two redox couples (fig. 4.8) are similar to those observed for p-dimethylamino-N,N-dimethylaniline (62) in figure 4.5.

The first redox wave indicates that the pendant electroactive redox groups are again oxidised to radical cations, with the wave shape being similar to that of compound (62). The second redox wave shows that the pendant redox groups can also be oxidized to the dication form, the potential position of this wave being similar to that of compound (62).

However for each of the three homopolymers, attempts to repeatedly scan the sample led to complete collapse of the redox signals. After a few cycles, the redox signal vanished completely (for example, fig. 4.9). If subsequently the working electrode was removed, its surface polished and then the CV recorded again, the two-redox couple CV similar to that in figure 4.8 was restored. This observation indicated that an insulating layer was deposited on the surface of the working electrode following the second oxidation peak. This insulating layer was found to be electro-inactive and could not be reduced. Even if it was maintained at -1.0 V for five minutes, activity was not restored. This also occurred on a platinum electrode, the change in electrode material failing to prevent the formation of the insulating layer.

In order to study what might have happened to the homopolymer during the second oxidation step, a glassy carbon electrode coated with a thin film of polymer (130) was maintained at 1.3 V for five minutes. This oxidised polymer film was found to be insoluble in ethyl acetate, though it did swell in this solvent, suggesting that it may have undergone crosslinking.

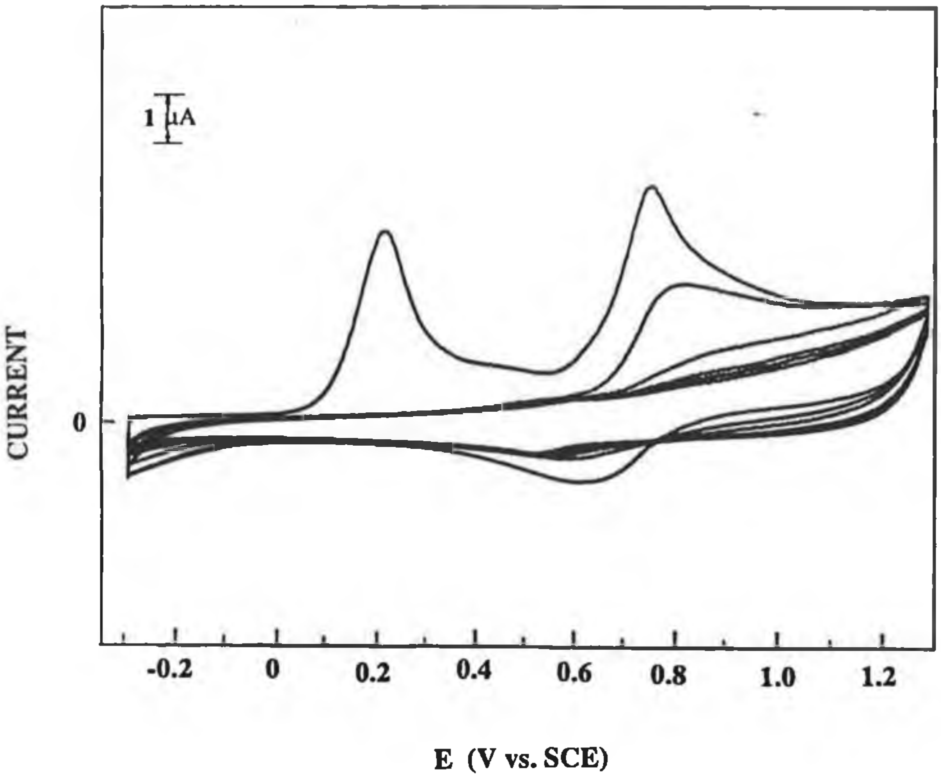
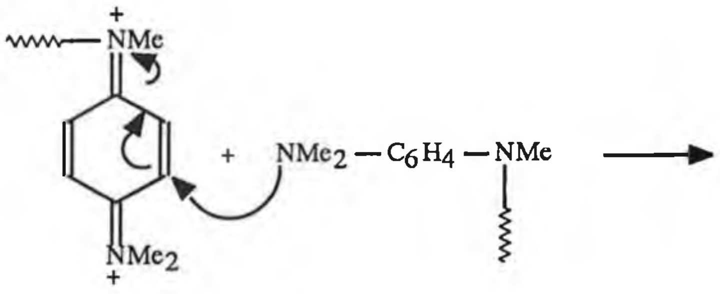
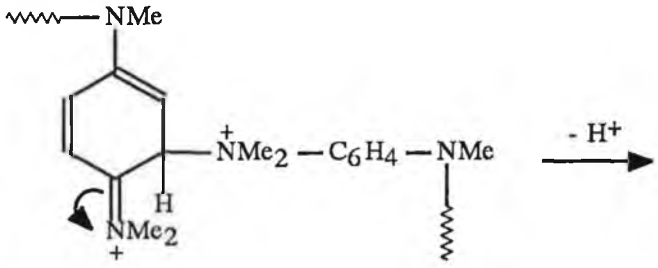


Figure 4.9 Cyclic voltammograms of polymer (130) in 0.1 M TEAP acetonitrile solution after the first scan, concentration of redox centres in the solution is 5.0 X 10^{-4} M, scan rate: 50 mVs^{-1}, glassy carbon electrode.

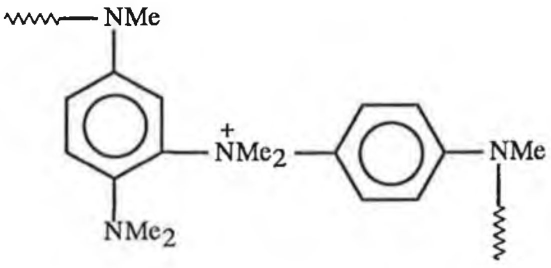
During the oxidation process, the diimine dications (149) formed might be expected to be susceptible to nucleophilic attack, possibly undergoing 1,4 - Michael addition reactions with any nucleophiles present. In the present case the active nucleophile could possibly be an adjacent unoxidized redox group (150) and such reaction could possibly lead to cross-linking of polymer chains as follows:



(149) (150)



(151)



(152)

Reactions such as this may have been responsible for crosslinking process resulting in the formation of insoluble polymers such as (152) and fouling of the electrode.

During the studies with compound (62) in acetonitrile solution (section 4.2.1), it was also noted that the two redox couples did decrease as the number of cycles increased but at a much slower rate than that for these homopolymers. The intramolecular distance between the centres in a polymer chain is however much smaller than for compound (62) in solution and this might explain this difference.

4.2.3 Spectroelectrochemical studies with the homopolymers

Conventional electrochemical measurements of current, potential, and charge only provide indirect information about the electrochemical changes of the redox groups. A combination of electrochemical and spectroscopic techniques might be expected to provide more direct information. The uv/vis spectra of p-dimethylamino-N,N-dimethylaniline (62) and its radical cation form (63) (Wurster Blue) have been reported.[180, 182] The difference between the two spectra is that for the radical cation there are two additional characteristic absorptions at 560 (ε, 11100) and 610 (ε, 11100) nm. The spectroelectrochemical technique has also been found useful in the investigation of electroactive polymer (130).

The spectrum of polymer (130) has no absorption bands from 400 to 800 nm. When the applied potential was maintained at 0.5 V, a broad absorbance from 450 - 650 nm appeared gradually (fig. 4.10).

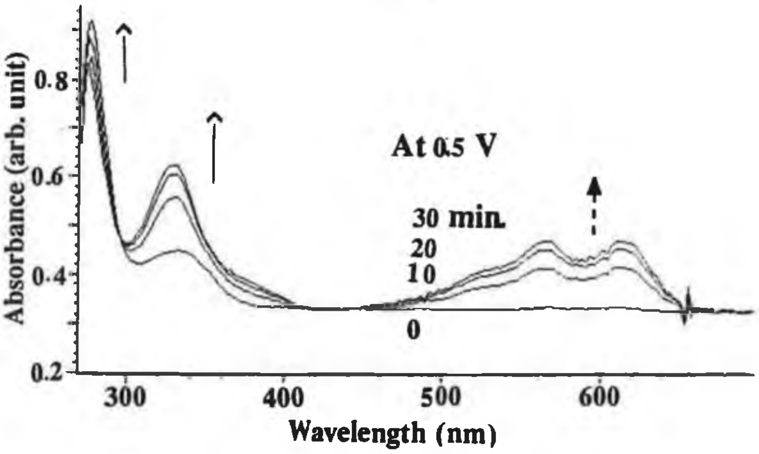


Figure 4.10 UV-Vis spectroelectrochemical spectra at 0.5 V, Concentration of redox centres of polymer (130) is 8.6 X 10^{-4} M, 0.1 M TEAP in propylene carbonate

At this potential, a blue colour developed in the cell, and the two absorption bands at 560 and 610 nm were similar to those of Wurster blue[183]. This spectrum confirmed that the pendant groups in the polymer were oxidised to the corresponding radical cation at 0.5 V.

Subsequently if the potential was swept back to -0.3V and maintained at this value, the absorptions at 560 and 610 nm decreased gradually and the original spectrum of polymer (130) was recovered (fig. 4.11). This indicated that the pendant groups on the polymer can be oxidised to the radical cation and subsequently reduced back to the neutral form reversibly.

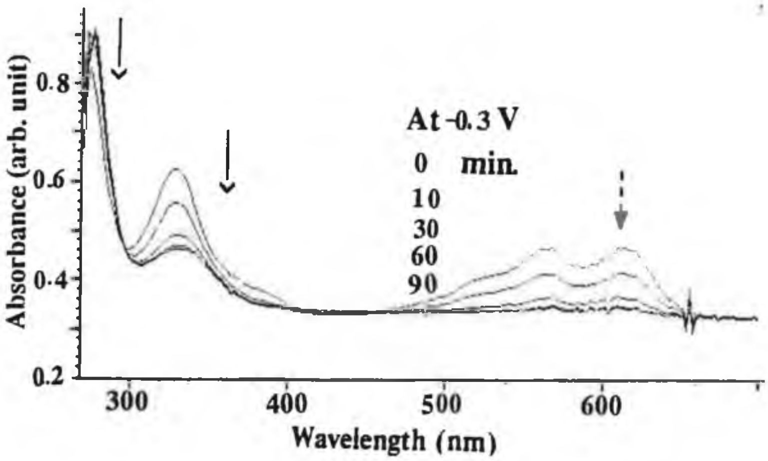


Figure 4.11 UV-Vis spectroelectrochemical spectra at -0.3V, Concentration of redox centres of polymer (130) is 8.6 X 10^{-4} M; 0.1 M TEAP in propylene carbonate

If the potential of a solution of (130) was swept to and maintained at -1.3 V, a broad absorption again appeared in the 450 - 650 nm range, However the original absorbance was no longer recoverable when the polymer was left at -0.3V. These observations also proved, spectroscopically, that for the two stage oxidation of the redox centres, the first redox couple is reversible but the second is not.

A parallel study of p-diaminomethyl-N,N-dimethylaniline (62) showed similar results. At 0.5V, absorptions at 560 and 610 nm appeared gradually (fig. 4.12). This reverts to the original spectrum by just maintaining the potential at -0.3V. At 1.3V, a strong broad absorption appeared in the 440 to 660nm region. However the original spectrum could not be recovered completely by resetting the potential at -0.3 V.

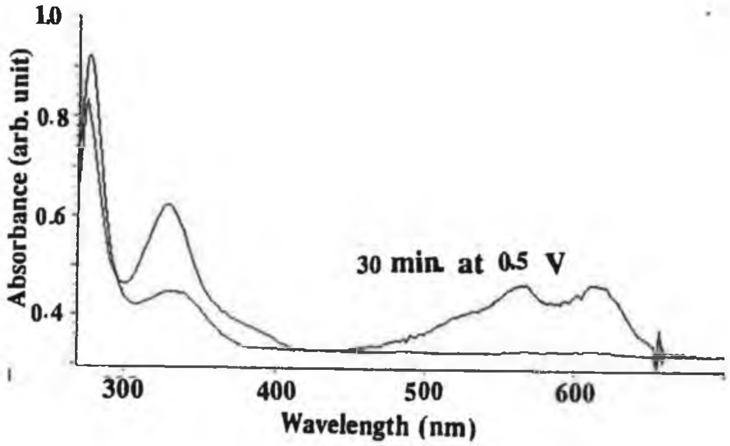


Figure 4.12 UV-Vis spectroelectrochemical spectra at 0.5 V, Concentration of compound (62) is 8.6 X 10^{-4} M; 0.1 M TEAP in propylene carbonate

4.2.4 Cyclic voltammetric studies for the copolymers with methyl acrylate

The polymers obtained by copolymerisation of the electroactive monomers (98), (101) and (104) with methyl acrylate are all soluble in acetonitrile and their electrochemical behaviour was investigated in this solvent. The first redox couples observed for these copolymers are similar to those of their corresponding homopolymers. They are also stable, and the normal potentials are identical to those of the corresponding homopolymers.

The two electron oxidation behaviour of the copolymers is slightly different from that of the homopolymers.

The two redox couple CV signal of the homopolymer can only survive two scans, and after this the signal vanishes completely (fig. 4.9). However, by contrast the two redox couple CV signals of the copolymers can survive a longer number of scans. The copolymers with methyl acrylate (10% and 5%) do show some improvement in stabilizing the second redox couple, but they can only last 5 or 6 more scans than the homopolymers (fig. 4. 13).

The use of copolymers therefore showed some improvement in respect of stabilizing the second redox couples but did not solve the problem completely.

The use of these homopolymers and copolymers to coat electrodes and thereby to permit investigation of their solid state electrochemical behaviour was attempted. However, the CV signal for the first redox couple for these polymers was not stable, due to rapid dissolution of the polymer into the acetonitrile or propylene carbonate solution phase.

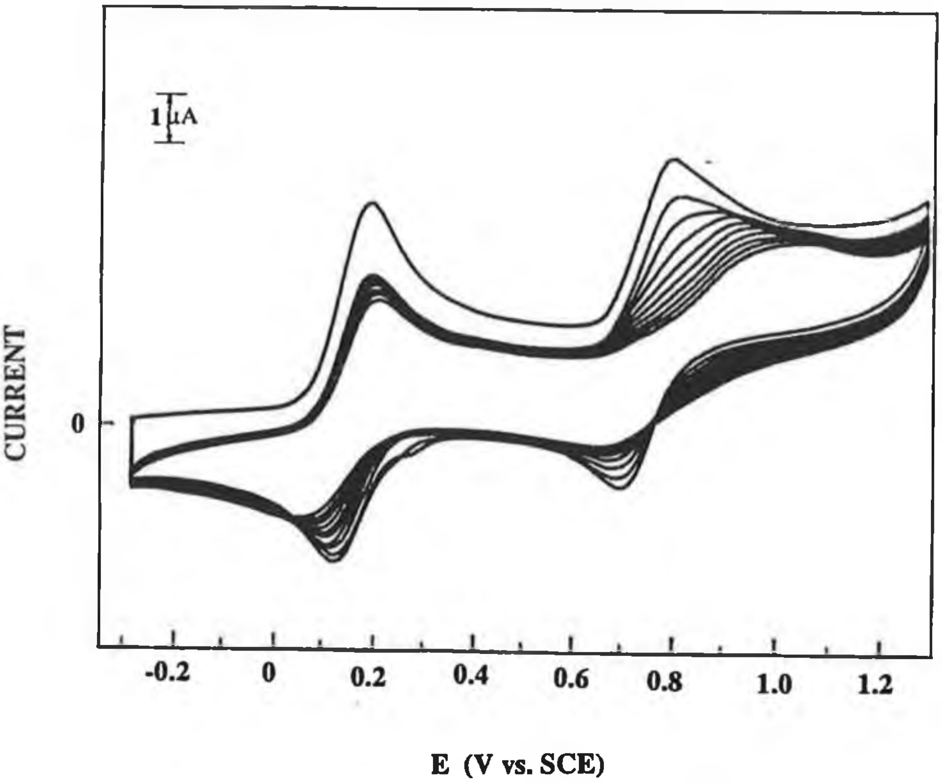


Figure 4.13 Cyclic voltammograms of a copolymer (138) (5%) in 0.1 M TEAP acetonitrile solution, concentration of redox centres in the solution is 4.5 X 10^{-4} M, scan rate: 50 mVs^{-1}, glassy carbon electrode.

4.2.5 Cyclic voltammetric studies of the styrene copolymers

The copolymers with styrene were insoluble in acetonitrile and propylene carbonate, and therefore their electrochemical behaviour could be investigated as solid coatings on modified electrodes. Although the styrene copolymers are not soluble in acetonitrile or propylene carbonate, they can be dissolved in some other common solvents, for example ethyl acetate or chloroform, and this makes it possible to coat the polymer on the surface of an electrode. Adhesion of the polymer films on a glassy carbon substrate was found to be better than that on a platinum substrate, therefore glassy carbon electrodes were used in all the experiments in this study.

Attempts to record the two oxidation step CV failed, because the CV signal collapsed completely in the second scan from -0.3 to 1.3 V. Figure 4.14 shows the first scan of the CV from -0.3 to 1.3V. The first oxidation peak appeared at about 0.15V, the second oxidation peak appeared at approximately at 0.65V, however, after the second oxidation step the polymer layer became completely inactive. The reduction process from 1.3 to -0.3V showed no signal, also a second scan of the CV from -0.3 to 1.3 showed no signal. All the styrene copolymers showed similar behaviour in the two step oxidation process, the CV signals collapsing completely after the second oxidation step.

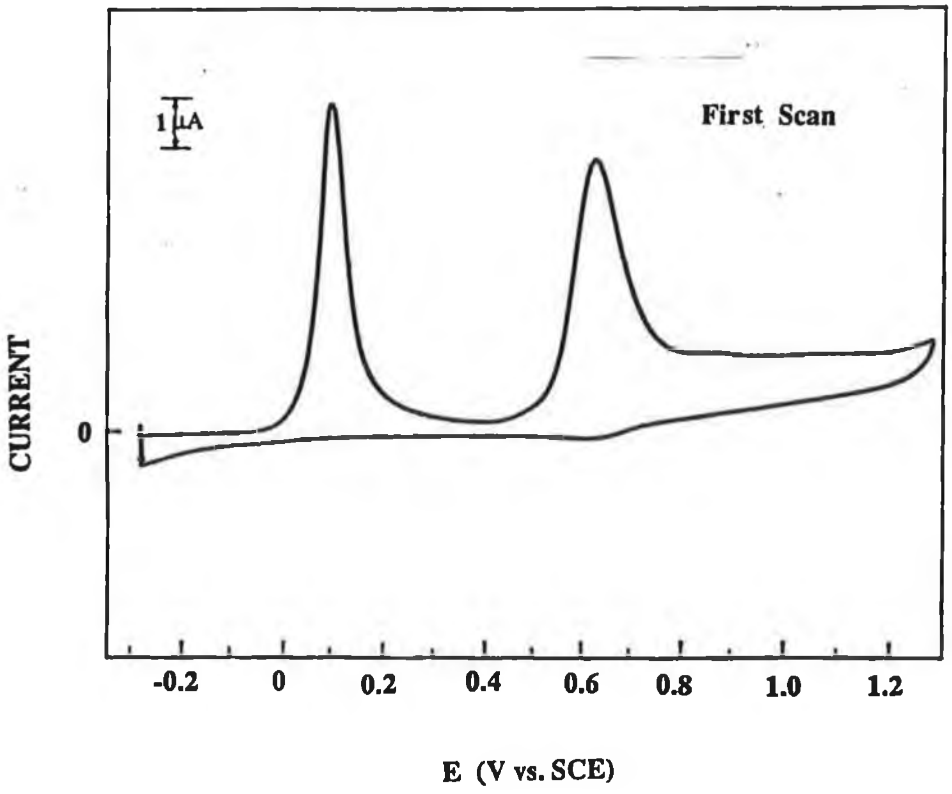


Figure 4.14 Cyclic voltammograms of polymer (130) coated glassy carbon electrode, scan rate: 10 mVs^{-1}, 0.1M TEAP in propylene carbonate

However if the potential sweep range was controlled from -0.3 to 0.5, the CV signal was stable. Therefore, further studies of these modified electrodes only limited to the first redox couple. Both acetonitrile and propylene carbonate proved good electrolyte solvents for these polymer modified electrodes. Details of the coating of the electrode are described in section 4.3.3. In acetonitrile, however the electrode is not stable with time, the peak height decreasing approximately ten percent after ten scans. A typical CV (figure 4.15) showed decrease of peak height with increasing number of scans. Even without scanning, the signal decreased slowly with the time exposed to the acetonitrile electrolyte solution. This instability of the electrode in acetonitrile could possibly be due to dissolution of the copolymers into the acetonitrile solution.

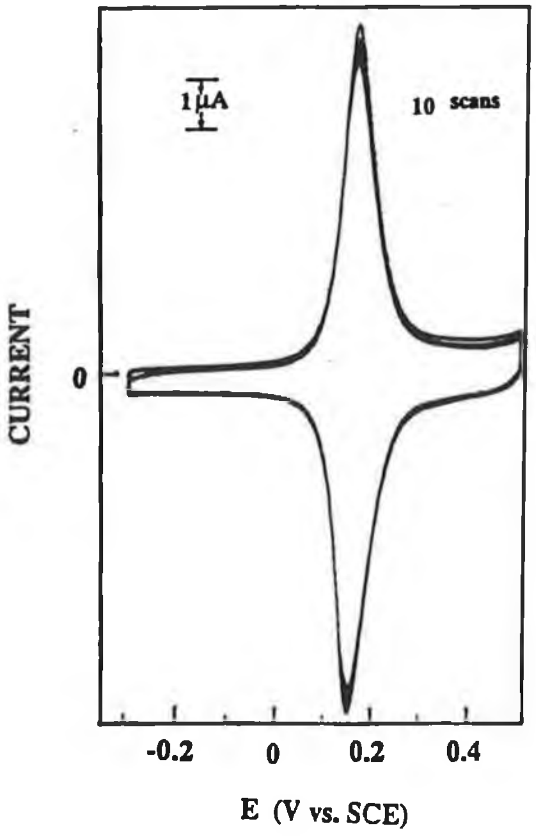


Figure 4.15 Cyclic voltammogram of copolymer (139) (20%) coated on glassy carbon electrode dipped in 0.1 M TEAP acetonitrile solution; scan rate 100 mVs^{-1}; $\Gamma = 1.7 \times 10^{-9}$ mol cm^{-2}, 10 scans.

With tetraethylammonium perchlorate in acetonitrile as the electrolyte solution the oxidation and reduction peaks are symmetric and sharp. A typical pattern of CVs at different scanning rates are shown in figure 4.16.

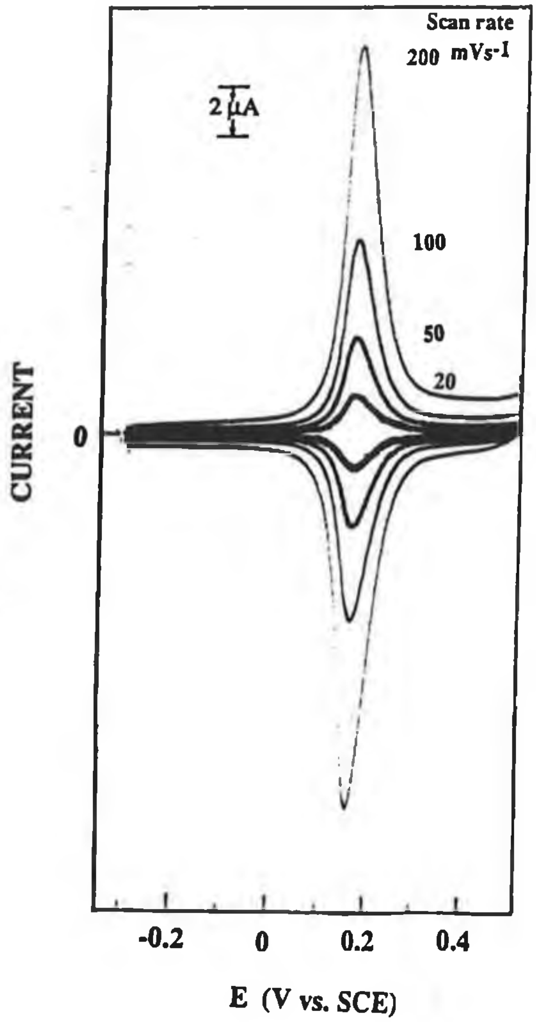


Figure 4.16 Cyclic voltammogram of copolymer (139) (20%) coated on glassy carbon electrode dipped in 0.1 M TEAP acetonitrile solution; at different scan rates; $\Gamma = 1.7 \times 10^{-9}$ mol cm^{-2}.

The CVs at different scan rates for all the copolymers were recorded (normally 2, 5, 10, 20, 50, 100, 200, and 500 mVs^{-1}). The peak heights were measured and plotted against the sweep rate. The analysed results are tabulated in table 4.2. Due to the relative instability of the polymer modified electrodes in acetonitrile solution, the reproducibility of the experiments was not very good.

Table 4.2 Cyclic voltammetry measurements of copolymers in 0.1M TEAP in acetonitrile as electrolyte

Polymer	normal potential[a] (V)	Charge coverage expected (molcm^{-2})	Charge coverage measured[b] (molcm^{-2})	Peak height vs. sweep rate is linear to (mVs^{-1})
139 (20%)	0.15 (0.01)[c]	1.0 (0.1)[c] X10^{-8}	1.7 (0.5)[c] X 10^{-9}	100
140 (5%)	0.20 (0.03)	1.0 (0.1)X10^{-8}	2.8 (2.2) X 10^{-9}	50
141 (15%)	0.15 (0.01)	1.0 (0.1)X10^{-8}	2.1 (0.8) X 10^{-9}	100
142 (5%)	0.20 (0.01)	1.0 (0.1) X10^{-8}	3.8 (1.7)X 10^{-9}	100
143 (15%)	0.12 (0.02)	1.0 (0.1)X10^{-8}	1.5 (0.5) X 10^{-9}	100
144 (5%)	0.15 (0.01)	1.0 (0.1)X10^{-8}	3.0 (1.1) X 10^{-9}	100

[a, b] Normal potentials and charge coverages were determined from the CVs at 2 mVs^{-1}.

[c] Errors calculated as standard deviation from the mean of, usually, determinations on three different films.

In table 4.2, the normal potentials of the low redox composition copolymers are higher than those of the higher composition copolymers, compare (139) and (140), 141) and (142), (143) and (144). The reasons for these differences are not clear. It probably is because of the different thicknesses and different bulk redox concentrations of the polymer films on the electrode. In applying polymer to give the same charge coverage, ie. the same number of redox centres, on the electrode, the film of the lower composition copolymer is thicker than that of the higher composition copolymer. Also the bulk concentrations of the redox centres are different in different composition copolymers.

Table 4.2 shows that the charge coverages measured electrochemically are always significantly lower than the expected values which is calculated from the amount of polymer placed on the electrode. Because these modified electrode are somewhat unstable in acetonitrile solution, there could be two reasons for the low charge coverage determined from the CVs. One is that the polymer film was dissolving into the acetonitrile solution. However even when the first scan (low scan rate) was used to determine the charge coverage, it was still significantly lower than that expected based on the amount added. Therefore dissolution of the polymer into the solvent is not likely to be the only reason for the low charge coverage measurements. Another reason could be that the redox centres in the polymer are not all active. Polystyrene is an insulator, and most of the copolymers are made up of styrene repeat units. If some redox centres are isolated from other redox centres and deeply trapped in these inactive styrene polymer segments, these redox centre will not be active due to lack of electron exchange with their environments.

When conducting higher scan rate experiments with the polymers mentioned in table 4.2, only the scan rates of 50, 100, 200, and 500mVs^{-1} were recorded. It was difficult to determine the exact position at which the peak height became non-linear with sweep rate. However, comparison of polymer (139) with polymer (140) (see table 4.2) showed that for the electrode modified with polymer (139) the peak height is linear with sweep rate to 100mVs^{-1}, whereas for the electrode with polymer (140) linearity does not extend beyond 50mVs^{-1}. The proportion of redox centres in polymer (139) is 20%, whereas the proportion in polymer (140) is 5%. The film of polymer (140) is much thicker than that of polymer (139) (to give the same coveraage with redox centres), therefore at sweep rate 100mVs^{-1}, the time scale is too short to fully oxidise the film of polymer(140), whereas at slower scan rates (< 50mVs^{-1}), complete oxidation of the available centres does occur.

In propylene carbonate (PC) the redox couple is perfectly stable. Figure 4.17 shows its stability for copolymer (139) in the TEAP/propylene carbonate system. Although only 50 scans are shown, actually there was less than a 10% decrease in peak height after 500 scans.

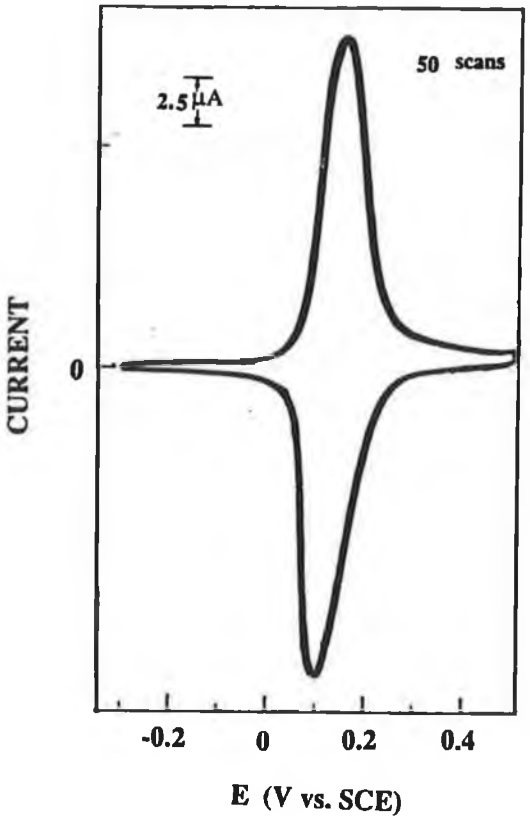


Figure 4.17 Cyclic voltammogram of copolymer (139) (20%) coated on glassy carbon electrode dipped in 0.1 M TEAP propylene carbonate solution; scan rate 100 mVs^{-1}; $\Gamma = 3 \times 10^{-8}$ mol cm^{-2}

Therefore in solid film form, the redox groups which are pendant on the polymer chains can be oxidised electrochemically to their radical cations and the radical cations can be reduced back to the neutral form in a reversible redox process.

Figure 4.18 shows the CVs of copolymer (139) (20%) at different scan rates in propylene carbonate. The peak height increased with increase in sweep rate as expected. The relationship between peak height and sweep rate is important, in attempting to understand the process occurring in the polymer film during oxidation/reduction.

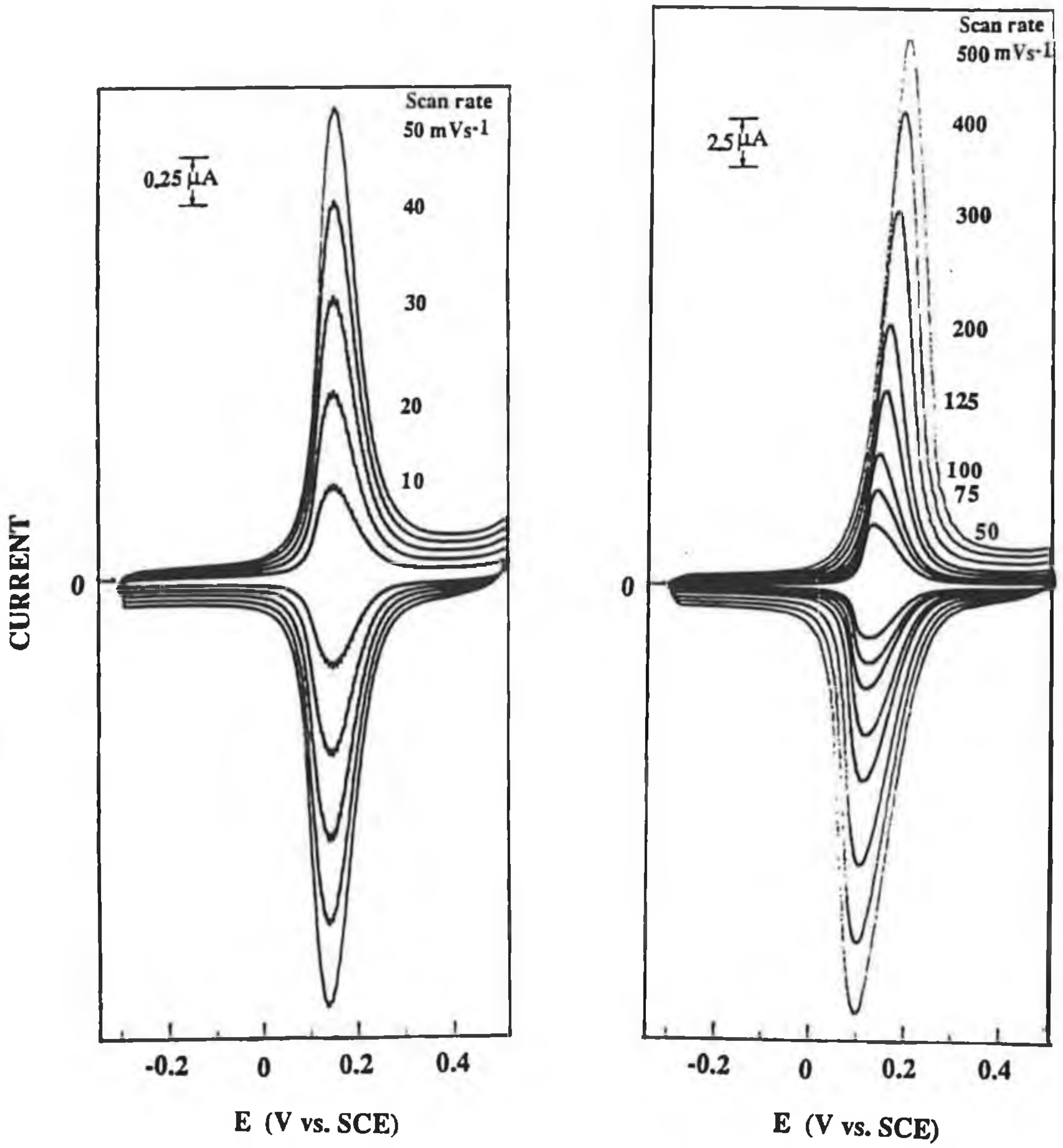


Figure 4.18 Cyclic Voltammogram of copolymer (139) coated on glassy carbon electrode dipped in 0.1 M TEAP propylene carbonate solution at different scan rates. $\Gamma = 8 \times 10^{-10}$ molcm^{-2}.

As mentioned in the introductory section, in surface behaviour the peak height should be linear with sweep rate; whereas in solution behaviour the peak height is linear with the square root of the sweep rate. For a polymer modified electrode, if the whole polymer layer is oxidised and reduced during one CV cycle, the polymer exhibits surface behaviour and obeys the surface behaviour laws;[5] if however only part of the polymer layer is oxidised and reduced, it exhibits solution behavior and obeys solution behaviour laws.[5]

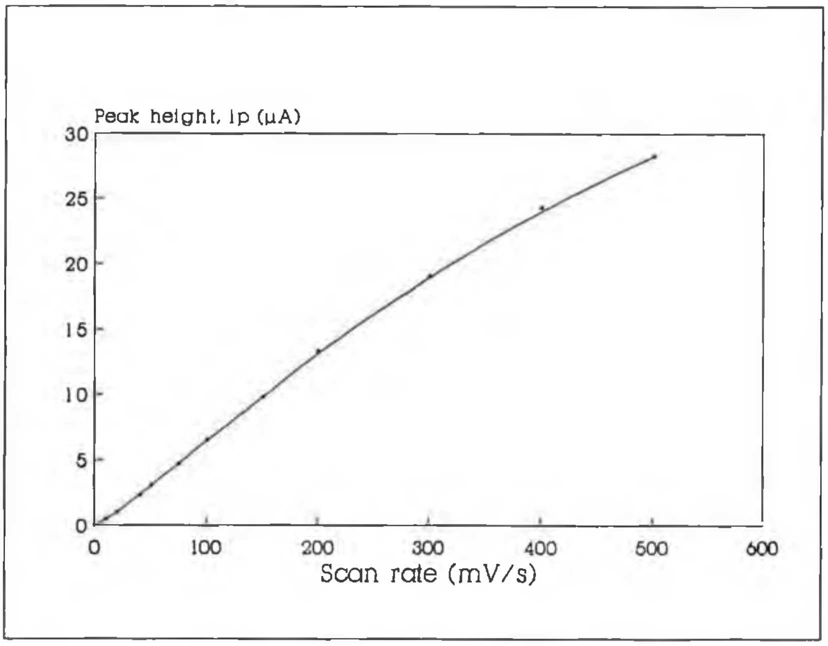


Figure 4.19 The relationship between peak height and scan rate for polymer (139)

Figure 4.19 shows the plot of the peak height against sweep rate for polymer (139) and from this figure it can be seen that at low sweep rates (10 to $150 mVs^{-1}$), the peak height increases linearly with the sweep rate, indicative of surface behaviour. Two other facts also support this conclusion. Firstly the peak-peak separations are close to zero at low scan rate, and secondly the full width at half-maximum is 90.6 mV (fig 4.18, low scan rates).

Figure 4.20 shows the plot of peak height against the square root of the sweep rate at higher sweep rates (150 to 500 mVs^{-1}). The relationship is linear, indicating solution behaviour over this range. With increasing sweep rate, the timescale become too short to allow the whole polymer layer to be fully oxidised and reduced during a cycle.. This is the reason why the peak height is no longer linear with sweep rate from 150 to 500mVs^{-1}.

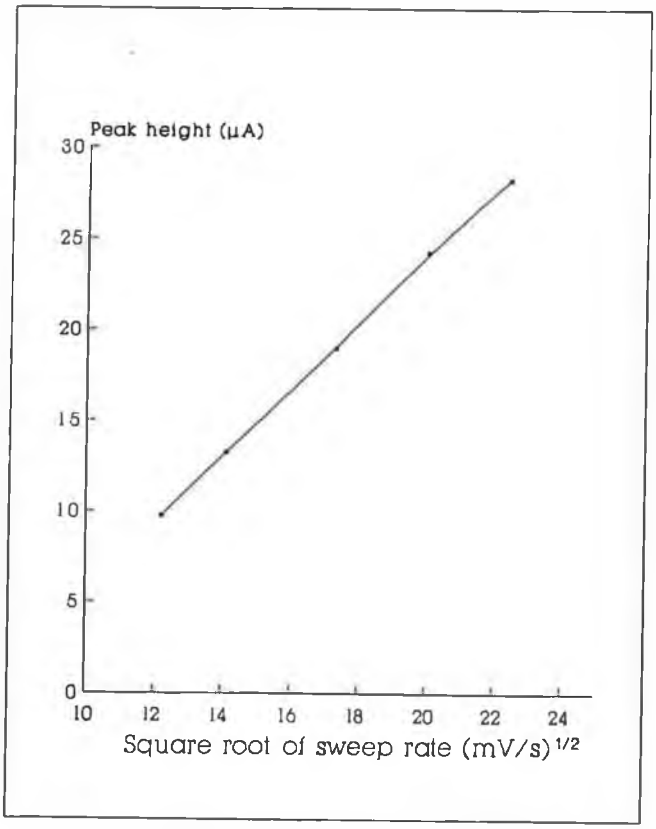


Figure 4.20 Plot of peak height against the square root of sweep rate at faster sweep rates (150 to 500 mVs^{-1})

The CVs at different sweep rates for all the styrene copolymers were investigated in propylene carbonate. The normal potential, charge coverage and peak height relationship sweep rate were analysed. The results are tabulated in table 4.3.

In this table the normal potentials for the different redox composition copolymers are again different. With the same copolymer different thicknesses, the modified electrode had the same normal potentials, therefore it can be concluded based on these results in table 4.3 that the normal potentials are dependent on bulk concentrations of redox centres not the thickness of the polymer films.

Table 4.3 Cyclic voltammetry measurements of copolymers in 0.1M tetraethylammonium perchlorate in propylene carbonate as electrolyte

Polymer	normal potential[a] (V)	Charge coverage expected (molcm^{-2})	Charge coverage measured[b] (molcm^{-2})	Peak height vs. sweep rate is linear to (mVs^{-1})
139 (20%)	(i) 0.15(0.01)[c]	1.0 (0.1)[c] X10^{-8}	1.7 (1.2)[c] X 10^{-9}	150
	(ii) 0.15 (0.01)	1.0 (0.1)X10^{-9}	2.3 (1.5)X10^{-10}	150
140 (5%)	(i) 0.18 (0.02)	1.0 (0.1)X10^{-8}	3.0 (0.8) X 10^{-9}	100
	(ii) 0.19 (0.02)	1.0 (0.1)X10^{-9}	3.5 (0.7)X10^{-10}	100
141 (15%)	(i) 0.15 (0.01)	1.0 (0.1)X10^{-8}	1.1 (0.2) X 10^{-9}	100
	(ii) 0.15 (0.01)	1.0 (0.1)X10^{-9}	3.9 (0.4) X10^{-10}	100
142 (5%)	(i) 0.19 (0.01)	1.0 (0.1) X10^{-8}	1.0 (1.0)X 10^{-9}	50
	(ii) 0.19 (0.01)	1.0 (0.1)X10^{-9}	3.1(1.4)X10^{-10}	100
143 (15%)	(i) 0.12 (0.02)	1.0 (0.1)X10^{-8}	1.5 (0.5) X 10^{-9}	100
	(ii) 0.13 (0.01)	1.0 (0.1)X10^{-9}	3.1 (1.3) X10^{-9}	100
144 (5%)	(i) 0.15 (0.01)	1.0 (0.1)X10^{-8}	4.5 (0.7) X 10^{-9}	100
	(ii) 0.15 (0.01)	1.0(0.1)X10^{-9}	4.6(0.9)X10^{-10}	100

[a, b] Normal potentials and charge coverages were determined from the CVs at 2 mVs^{-1}.

[c] Errors calculated as standard deviation from the mean of, usually, determinations on three different films.

The charge coverages measured by the low scan rate (table 4.3), are all significantly lower than the amount applied to the electrode. In the propylene carbonate system, the electrodes modified with the styrene copolymers are very stable, and it can therefore be concluded that the origin of this difference is that the redox centres in the polymer films are not all active. It could be because some redox centres are isolated into inactive polystyrene segments, and they are too far away from the other redox centres for exchange of electron to occur. Also these redox centres could be so deeply trapped in the polystyrene segments that electrolyte solution could not permeate through. Table 4.3 shows that for a specific copolymer, in a thicker film the proportion of inactive redox centres is higher than in a thin film.

In most of the experiments listed in table 4.3 the sweep rates used were 2, 5, 10, 20, 50, 100, 200, and 500 mVs^{-1}. Comparison of copolymer (139) with (140) and copolymer (141) with (142) suggests that the peak heights for higher redox composition copolymers are linear with sweep rate to over a larger sweep rate range than is observed for lower redox composition copolymers. With the same charge coverage, low redox composition layers are thicker than the higher redox composition layers on the electrodes, therefore a longer time is needed to oxidise or reduce fully the polymer layer for the lower composition copolymer.

The plot of peak height against sweep rate curved beyond the highest linear sweep rates (shown in table 4.3). Because most of my results were only recorded in 100, 200, 500mVs^{-1}, the detailed discussion of these higher sweep range behaviour is difficult.

Due to the incomplete oxidation/reduction of the redox centres in the polymer layer, the assessment of the thermodynamic parameters of these modified electrode became impossible. The theory does not apply in these cases.

Lithium perchlorate was found to be as effective a supporting electrolyte as tetraethylamonium perchlorate for these redox polymers in propylene carbonate and the copolymer modified electrodes were as stable as in TEAP propylene carbonate electrolyte. Figure 4.21 shows typical CVs at different scan rates.

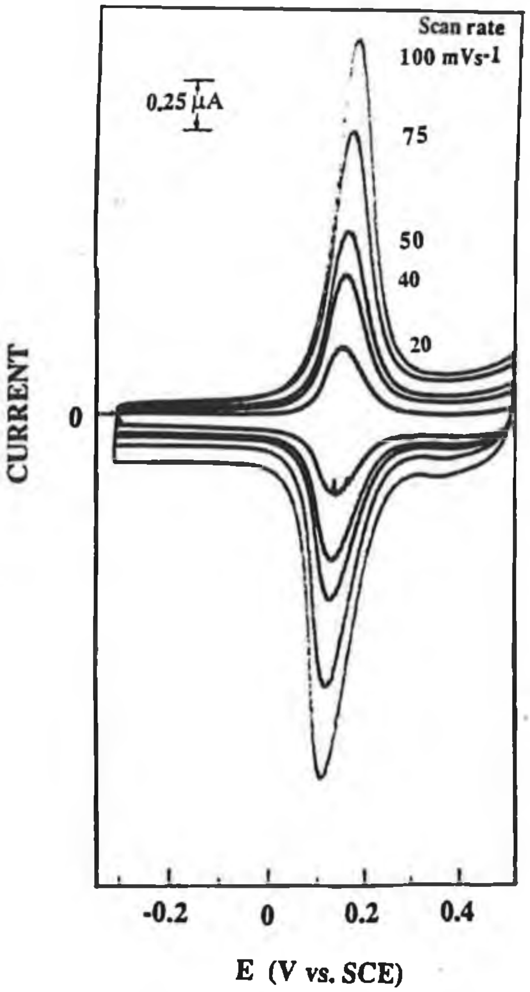


Figure 4.21 Cyclic voltammogram of copolymer (139) (20%) coated on glassy carbon electrode dipped in 0.1M lithium perchlorate propylene carbonate solution; at different scan rates; $\Gamma = 4.5 \times 10^{-10}$ mol cm^{-2}.

Only three copolymer modified electrodes were examined with lithium perchlorate as supporting electrolyte. Their behavior was similar to that reported above for TEAP in propylene carbonate. The charge coverages measured electrochemically were again significantly lower than expected on the basis of the amount placed on the electrode.

The stable behaviour of the copolymer modified electrodes in the lithium perchlorate in propylene carbonate electrolyte system is of great importance if these polymers are to find application in rechargeable batteries, because this electrolyte system is commonly used in the lithium rechargeable battery.[89]

4.2.6 Investigation of mediation by the electroactive polymers

Mediation means the transfer of electrons from an electrode to a solution species via surface-immobilized redox centres. The fundamental reactions which occur between a solution species Y, with Z being the reduced product of Y, and a mediating layer containing the redox couple A/B can be described by reactions (4.6) and (4.7)

$$B - e \longrightarrow A \qquad (4.6)$$

$$A + Z \longrightarrow B + Y \qquad (4.7)$$

In this example the mediating process involves oxidation of the surface bound species B, but the same principles hold for the reduction process also.

The phenomenon of mediation is important in electroanalysis using modified electrodes. The rotating disk technique[184] is commonly used for the investigation of mediation. This is similar to cyclic voltammetry except that the working electrode is rotated in the electrolyte solution at a certain speed. Typical rotating disk responses are shown in figure 4.22 (a) and (c). In order to detect mediation between the polymer film on the electrode and a redox species in the electrolyte solution, the following experiments are carried out (fig. 4.22).

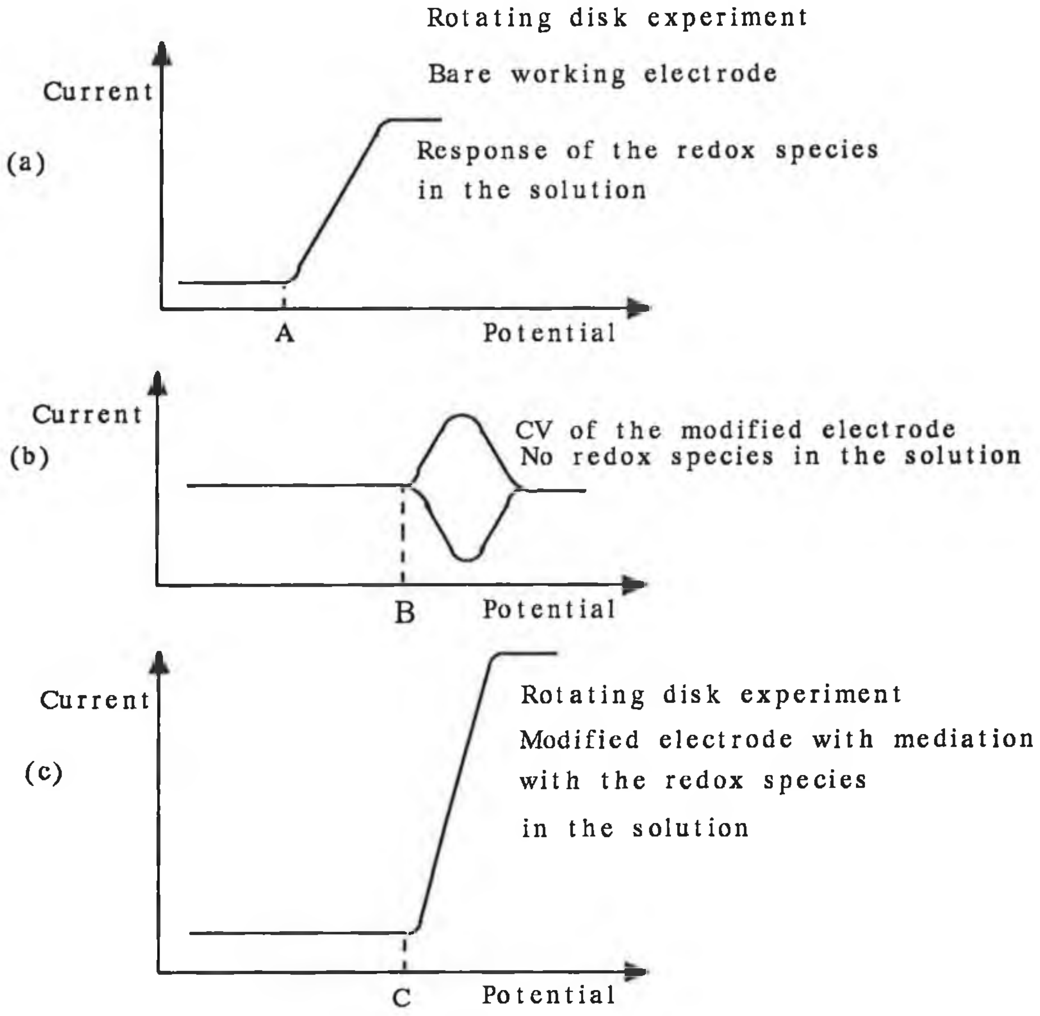


Figure 4.22 Experiments for the investigation of mediation by a modified electrode

Firstly, a redox species whose mediation is to be investigated is dissolved in the electrolyte solution with a supporting electrolyte, and its rotating disk signals are recorded at different rotation speeds with a bare working electrode [fig. 4.22 (a)]. Secondly, the CV of the modified electrode in the same electrolyte solution but in the absence of the redox species is recorded [fig. 4.22 (b)].

If the normal potential of the redox polymer coated on the electrode is higher than the normal potential of the redox species in the solution as is the case in figures 4.22 (a) and (b), mediation may be possible and can be investigated using another rotating disk experiment.

In this third experiment, the redox species of interest is dissolved in the electrolyte solution, and the working electrode is coated (or modified) with the electroactive polymer under investigation. Until the potential reaches the point C the polymer layer is inactive, and there is therefore no current response although the potential is in principle high enough to oxidise the redox species in the solution. At potential C however the polymer layer becomes active and, if there is mediation between the electroactive polymer on the electrode and the redox species in the solution, a more intense rotating disk response should appear [figure 4.22 (c)]. The intensity of the observed signal is greater than in situation (a) since it is due to both the redox species in solution and the electroactive polymer on the electrode.

Ferrocene is soluble in propylene carbonate, its normal potential vs SCE in propylene carbonate with lithium perchlorate as supporting electrolyte being determined as - 0.05V. The normal potential of copolymer (139) vs SCE is 0.15V. However rotating disk experiments with an electrode modified with this polymer and with 0.1M ferrocene in the electrolyte solution did not give the expected response. The observed current intensity was identical to that of the modified electrode alone, indicating no mediation of ferrocene redox activity by the polymer. The failed mediation is most likely due to the low activity of the redox centres in the polymer film. From table 4.3, it can be seen that only a fraction of the redox centres in polymer film (139) are active, these active centres possibly being those close to the electrode surface. Redox centres in the middle of the polymer film may possibly not be active due to poor conductivity through the bulk of the polymer, and thereby contribute to the barrier for charge transfer to the polymer-solution interface.

Of possible candidates for successful mediation, ferrocene was the only one found to be soluble in propylene carbonate.

Most of the soluble redox species commonly investigated are used in aqueous solution. However, the electrochemical signals of the redox polymers investigated in this study are not stable under aqueous conditions. In the presence of aqueous electrolyte, the normal potential of the first redox step is very close to that of the second one, and it is difficult to obtain a stable one electron redox couple. Using aqueous electrolyte, all the homopolymers, copolymers with methyl acrylate and copolymers with styrene can stay on the electrode.

Figure 4.23 shows a typical CV signal of an homopolymer in aqueous electrolyte, and this CV decreases gradually as the number of cycles increases.

The normal potential of ascorbic acid in aqueous electrolyte solution is lower than that of the redox couple in Figure 4.23. However attempted mediated oxidation of ascorbic acid in aqueous electrolyte using an electrode modified by polymers (130) (134) did not succeed. Mediation oxidation of potassium ferrocyanide and ammonium iron (II) sulphate were also investigated, but without success. The reason for the failure to observe mediation under aqueous conditions is probably due to the instability of the modified electrode in water. The CV signal decreases as the number of scans increases. When the electrode was rotating, the signal of the modified electrode decreased much more quickly.

These failures to observe mediation with polymer (130) (134) suggests that these electroactive polymers are not suitable for application in electroanalysis.

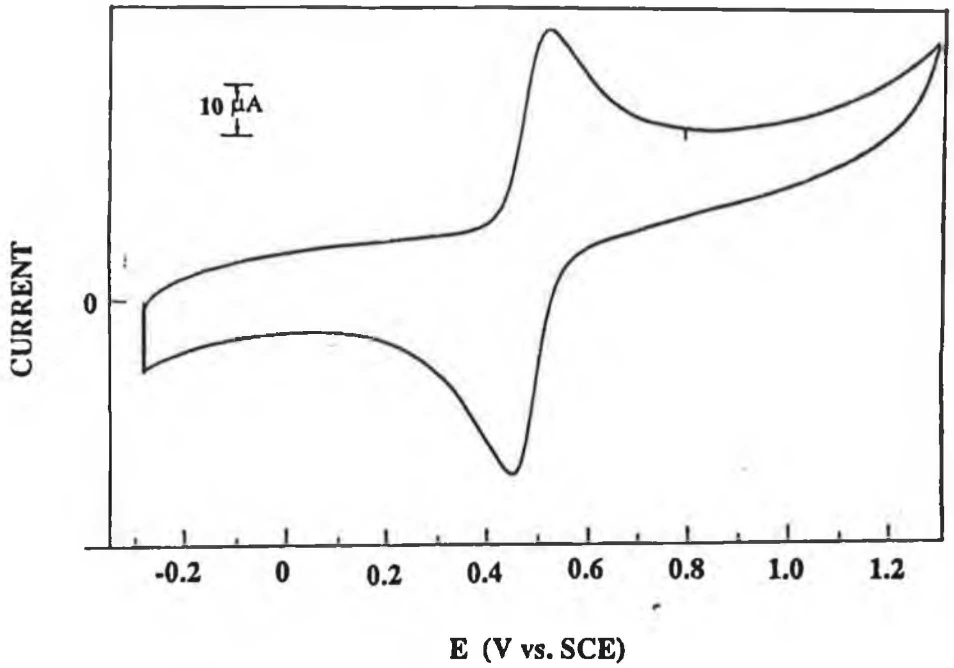


Figure 4.23 Cyclic voltammogram of polymer (130) coated on a glassy carbon electrode, scan rate: 10 mVs^{-1}, 0.2 M aqueous perchloric acid solution.

4.2.7 Some suggestions for application of these electroactive polymers

In the solid state, the styrene copolymers have a very stable redox couple and can be repeatedly scanned from -0.3 to 0.5V (vs SCE) in lithium perchlorate/propylene carbonate. This electrolyte system is commonly used in the manufacture of lithium rechargeable batteries. It would seem possible therefore that the styrene copolymers might have potential for use as electrode materials for rechargeable battery use with this electrolyte medium. However the incomplete oxidation/reduction of the redox centres in the polymers is a disadvantage of these polymers. Some improvement in conductivity of these polymers is needed before use as battery material, for example, making blend with carbon black, or some conducting polymers.

The homopolymers and the copolymers with methyl acrylate are all soluble in propylene carbonate. They also exhibit long term stability when repeatedly scanned over the range from -0.3 to 0.5V vs SCE. A conductive separator between the electrolyte system and the solid redox polymer would be required if propylene carbonate were to be used in the electrolyte system for a battery using these polymers.

The homopolymers, the copolymers with methyl acrylate, and the copolymers with styrene are all electrochromic materials. The colourless polymer can be oxidised electrochemically to yield a blue derivative, and this blue derivative material can be reduced back to the colourless form using an applied potential in the range -0.3 to 0.5V vs SCE. These electrochromic materials might provide the basis for the construction of display devices.

4.3 Experimental section

4.3.1 Cyclic voltammetry

Analar grade acetonitrile and propylene carbonate dried over molecular sieves 4A were used in the electrochemical measurements. Tetraethylammonium perchlorate (TEAP) (recrystallized three times from water and dried) and Analar grade lithium perchlorate were used as electrolytes. A 3 mm diameter Teflon shrouded glassy carbon electrode was used as the working electrode and a platinum net as auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE). Electrochemical cells were of conventional design. For the CV measurement of solutions, the cell was a three compartment cell. The three compartment solution cell used for this study is illustrated in figure 4.24. The polymer is dissolved in the electrolyte solution in the compartment containing the working electrode and the compartments containing reference electrode and auxiliary electrode contain only electrolyte solution. CV measurements were performed using an EG & G Model 273 Potentiostat/Galvanostat.

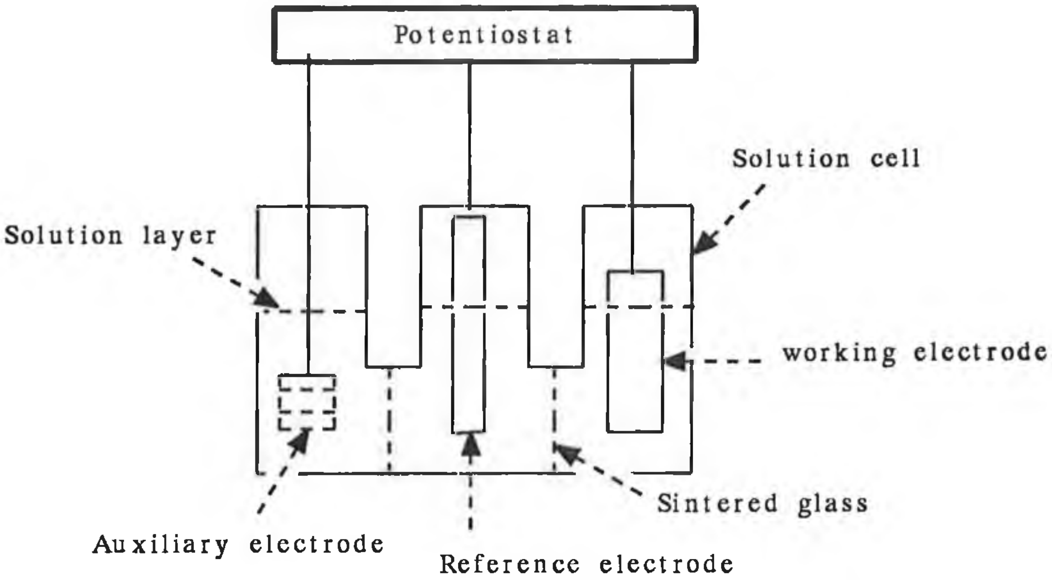


Figure 4.24 Schematic diagram for the cyclic voltammetric experiment in solution

For the study of modified electrode, the arrangement used in the cyclic voltammetric experiments is illustrated in figure 4.25

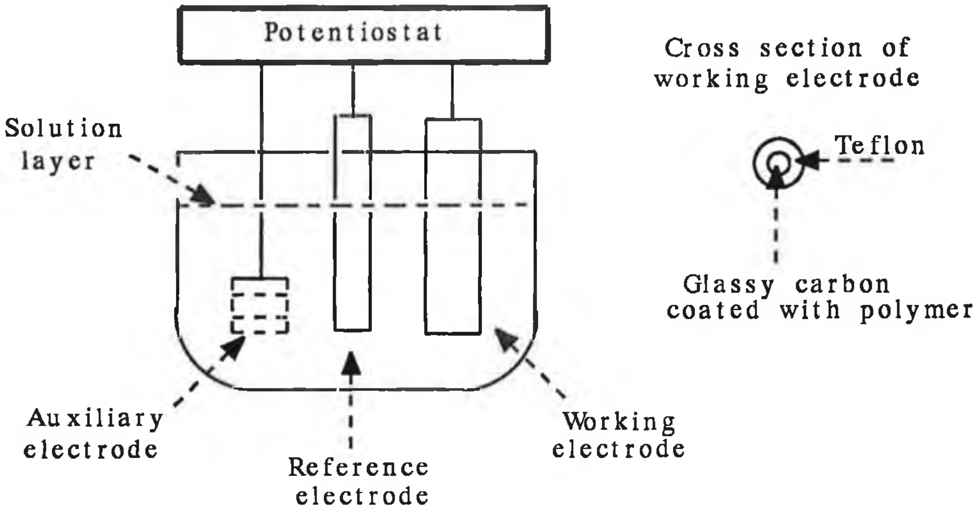


Figure 4.25 Schematic diagram of cyclic voltammetric apparatus for use with the polymer modified electrodes.

CV measurements were performed using an EG & G Model 273 Potentiostat/Galvanostat.

4.3.2 Determination of surface coverages

Using the slow sweep rate cyclic voltammograms (2 mV/s), the area of the CV peak was determined by weighing traced uniform paper. The weight of 1cm^2 uniform paper is 8 mg, therefore the area of the CV peak can be determined. The charge (Q) on the electrode will be:

$$Q = B\ I\ V/\upsilon \tag{4.8}$$

where B is the area of the CV peak (cm^2), I is Y axis scale(the current per centimetre, Acm^{-1}), V is the X axis scale (the voltage per centimetre, Vcm^{-1}). υ is the sweep rate (Vs^{-1}).

The surface coverage (Γ) can be determined using equation 4.5, from the relationship $\Gamma = Q/nFA$, where Q is the charge on the electrode, n is the number of charges transferred, F is the Faraday constant, and A is the area of the electrode.

4.3.3 Preparation of electrode

Firstly, the surface of the glassy carbon electrode was polished with 0.5 μm aluminia slurry on a felt cloth. This was continued until a perfect mirror finish was obtained, then the surface of the electrode was washed with deionised water and methanol and dried. The background of the electrode was checked electrochemically prior to modification and electrochemical measurement. For preparation of a modified electrode, following this pretreatment of the glassy carbon electrode, 5 μl of an ethyl acetate copolymer solution of a particular concentration was dropped on the surface of the electrode which was then air dried. The concentration of the redox centres in the solution for $\Gamma=10^{-8}molcm^{-2}$ coating is $1.41X10^{-4}M$, 5μl of this solution was dropped on the surface of the electrode. For the $\Gamma=10^{-9}molcm^{-2}$ coating, the concentration of redox centres in the solution was $1.41X10^{-5}M$, 5μl of this solution was dropped on the surface of the electrode.

4.3.4 UV - Visible spectroelectrochemistry

The spectroelectrochemical experiment and the electrochemical cell used are illustrated in figure 4.26.

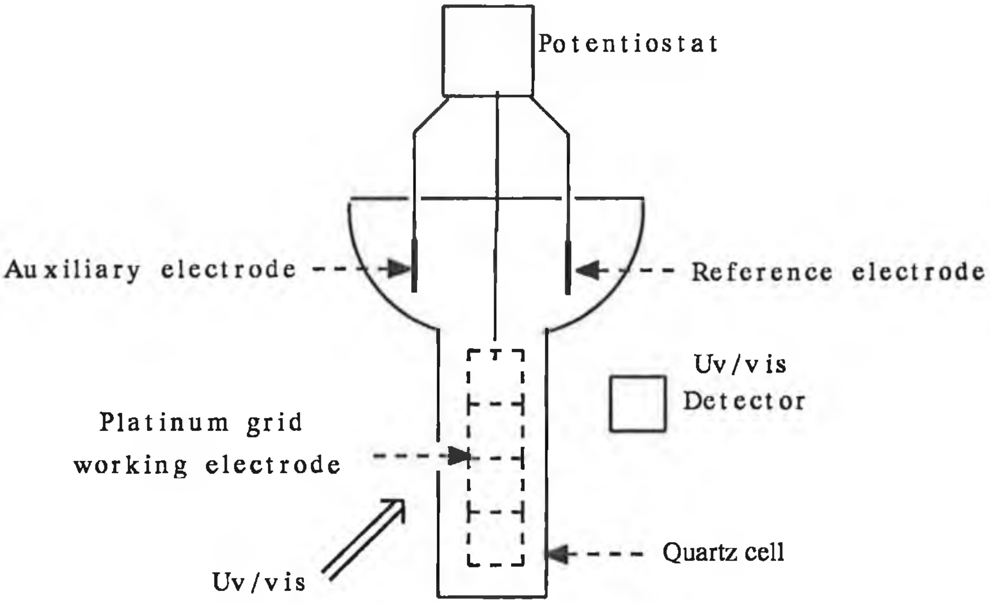


Figure 4.26 Schematic diagram of spectroelectrochemical experiment

In this experiment, polymer (130) and supporting electrolyte TEAP were dissolved in propylene carbonate and placed in the quartz cell. The applied potential was controlled by the potentiostat through the electrodes and the resulting chemical changes of the polymers in the solution were followed using a uv/visible spectrophotometer.

The thickness of the quartz cell is 1mm. The working electrode was a platinum grid inserted into the optical path of the cell. The reference (Ag/AgCl) and auxiliary (platinum wire) electrodes were placed in the solution in the upper part of the cell (an electrolyte solution reservoir).

An EG & G Model 363 Potentiostat/Galvanostat and Hewlett Packard 8452A diode array UV-Visible spectrophotometer were used to generate the electrochemical intermediates and to measure the spectra respectively.

4.3.5 Rotating disk experiments

A rotating-disk electrode constructed of glassy carbon of 3 mm diameter (Metrohm) and a Metrohm 628-10 Rotator were used for the rotating disk experiment. The potentiostat was the same as for the cyclic voltammetry measurements.

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